Fig. 2. Projection of the unit cell along the *b* axis.

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carbonyls is roughly perpendicular to that of the methoxymethyl chain. The plane of the three C(sp^3) atoms in the ring and two methyl substituents forms angles of 52·6 (5), 126·4 (5)° with the carbonyl and methoxymethyl mean planes, respectively. O(12) is thus in a favorable position with respect to H(51) of the same molecule: angle O(12)–H(51)–C(5) 123·6 (13°, distance O(12)–H(51) 2·41 (2) Å.

Crystal packing shown in projection along the *b* axis in Fig. 2 is mainly determined by van der Waals interactions. No intermolecular distances shorter than the sum of van der Waals radii were observed.

Structure of 2,2-Dimethyl-1,3-dioxane-4,5,6-trione 5-(2,4-Dinitrophenylhydrazone), $C_{12}H_{10}N_4O_8$

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Abstract. $M_r = 241·25$, monoclinic, $P2_1/c$, $a = 14·236 (12)$, $b = 5·220 (5)$, $c = 20·111 (15)$ Å, $\beta = 99·4 (1)°$, $V = 1474·4$ Å^3, $Z = 4$, $D_x = 1·32$, $D_m = 1·35 (1)$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1·00$ cm^{-1}, $F(000) = 460$, room temperature, final $R = 0·072$ for 1089 independent observed reflections. In the structure the amine hydrogen atom H(7) forms a bifurcated intramolecular hydrogen bond to the *ortho*-nitro group and to a carbonyl oxygen atom. The two H(7)···O distances are equivalent within experimental error. The N(8)–C(9)–C(10) angle is larger than the N(8)–C(9)–C(20) angle by almost 15° so that this bond can be accommodated. The dioxane ring is in the envelope conformation.

Introduction. Our studies of the structural chemistry of phenylhydrazones have shown that the amine hydrogen atom H(7) has a strong proclivity to intramolecular

† Deceased.

hydrogen bonding either to a suitable *ortho*-substituent on the aromatic ring, *e.g.* $R^1 = NO_2$ (*A*), or a suitable α-oxo group, *e.g.* $R^3 = {>}C{=}O$ (*B*); with both present a three-centre bifurcated hydrogen bond can be formed (*C*) (Vickery, Willey & Drew, 1981*a*).
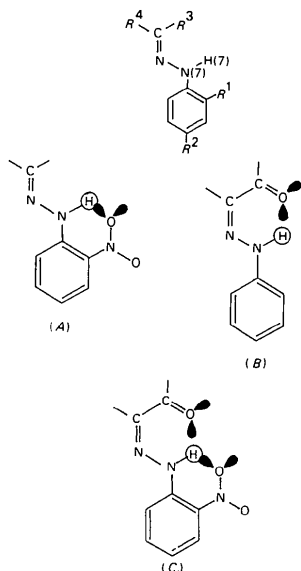
The driving force for such hydrogen bonding can be attributed to the six-membered-ring formation resulting from a preferred directionality of the sp^2 lone pairs of electrons associated with the binding oxygen atoms. Certainly replacement of an NO_2 group by the strongly electronegative but monofunctional chlorine atom at R^1 does not result in N—H⋯Cl bond formation (Drew, Vickery & Willey, 1981). In the absence of such strategic $-NO_2$ or C=O groups at R^1 and R^3 respectively, much weaker intermolecular hydrogen bonding linking H(7) and either a solvent molecule or a suitable donor substituent, *e.g.* $R^2 = NO_2$, of an adjacent molecule has been demonstrated (Willey & Drew, 1983).

The structures of two phenylhydrazone derivatives of Meldrum's acid, namely (2) and (3), have been previously described (Vickery, Willey & Drew, 1981*b*). Here we report the structure of another molecule in the series, namely the title compound (1) with $R^1 = R^2 = NO_2$.
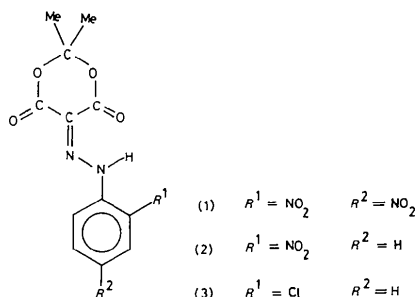
This structure provides a useful comparison with these others and also offers a rare example of a bifurcated intramolecular hydrogen bond whose geometries have been discussed recently (Taylor, Kennard & Versichel, 1984). We compare the conformation of the bifurcated hydrogen bond in (1) and (2) and also in the related compound dimethyl 2-(2,4-dinitrophenyl-hydrazono)propanedioate (structure 4 in Vickery *et al.*, 1981*a*).

Experimental. Compound (1) was prepared following the procedure as described previously (Vickery *et al.*, 1981*b*). Suitable crystals were obtained following recrystallization from methanol–dichloromethane solutions and placed in Lindemann tubes. Density measured by flotation. Crystal, approximate size 0·3 × 0·5 × 0·2 mm, mounted on a Stoe STADI2 diffractometer to rotate about the *b* axis. Cell dimensions obtained by measurement of *ca* 20 high-angle axial reflections. Intensity data collected *via* variable-width ω scan, background counts 20 s, step-scan rate of 0·033° s⁻¹ applied to a width of $(1·5 + \sin \mu/\tan\theta)°$; $2\theta_{max} = 45°$. Absorption and extinction corrections not applied. Standard reflections 2*k*2 measured every 20 measurements for each layer; no significant change in intensity. 2930 reflections measured ($-18 < h < 14$, $0 < k < 5$, $0 < l < 23$) of which 1096 independent data with $I > 2\sigma(I)$ refined (on *F*) to $R = 0·072$ ($wR = 0·076$, $S = 2·30$). Weighting scheme $w = 1/[\sigma^2(F) + 0·03F^2]$ chosen to give similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F_o, $\sigma(F)$ from counting statistics. Structure solved using *MULTAN*80 (Main *et al.*, 1980). H atoms included in calculated positions and their thermal parameters refined. The position of H(7) was, however, allowed to refine. Hydrogen atoms on the same carbon atom given an equivalent thermal parameter. Non-hydrogen atoms refined anisotropically *via* full-matrix least squares. Scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Final difference-Fourier maps showed no important features and in final cycles of refinement no shift $> 0·1\sigma$. Calculations carried out using *SHELX*76 (Sheldrick, 1976) at the University of Manchester Computer Centre.

Discussion. Final coordinates are given in Table 1, molecular dimensions in Table 2.*

The structure of (1) is shown in Fig. 1 together with the atomic-numbering system. As expected there is a bifurcated intramolecular hydrogen bond between H(7)

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* Lists of structure factors, anisotropic thermal parameters and hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39932 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and an oxygen of the *ortho*-nitro group O(3) and a carbonyl oxygen O(11).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}_{eq}$*(Å^2)
C(1)	2346 (5)	−1750 (17)	6434 (4)	74 (9)
C(2)	2712 (4)	245 (17)	6830 (4)	84 (9)
C(3)	3604 (4)	1155 (13)	6761 (3)	60 (7)
C(4)	4150 (4)	−67 (13)	6309 (3)	59 (7)
C(5)	3733 (5)	−2055 (17)	5934 (4)	72 (8)
C(6)	2845 (5)	−2921 (15)	5985 (4)	64 (8)
N(7)	5050 (4)	817 (12)	6248 (3)	60 (6)
N(8)	5544 (4)	−591 (12)	5875 (3)	60 (6)
C(9)	6417 (4)	168 (14)	5847 (3)	69 (7)
C(10)	6912 (5)	2348 (18)	6188 (4)	81 (9)
O(11)	6531 (4)	3973 (10)	6477 (3)	78 (6)
O(12)	7831 (3)	2586 (11)	6119 (3)	92 (7)
C(13)	8351 (5)	390 (15)	5976 (4)	83 (8)
C(14)	9249 (6)	1358 (23)	5730 (7)	131 (14)
C(15)	8546 (5)	−1281 (20)	6584 (4)	90 (11)
C(20)	6890 (5)	−1485 (17)	5401 (4)	72 (8)
O(21)	6508 (4)	−3127 (11)	5030 (4)	76 (6)
O(22)	7817 (3)	−966 (12)	5412 (3)	88 (7)
N(2)	1410 (5)	−2700 (16)	6533 (5)	95 (10)
O(3)	1007 (5)	−1753 (18)	6950 (4)	131 (11)
O(4)	1097 (5)	−4553 (22)	6178 (5)	140 (14)
N(1)	3948 (4)	3325 (12)	7168 (3)	69 (7)
O(1)	4714 (4)	4309 (11)	7122 (3)	77 (6)
O(2)	3432 (4)	4191 (13)	7554 (3)	96 (8)

$$* \ \bar{U}_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

Table 2. *Bond distances* (Å) *and angles* (°)

C(1)—C(2)	1·362 (12)	N(7)—N(8)	1·330 (8)
C(1)—C(6)	1·379 (11)	N(8)—C(9)	1·315 (8)
C(1)—N(2)	1·466 (11)	C(9)—C(10)	1·451 (11)
C(2)—C(3)	1·385 (10)	C(9)—C(20)	1·482 (11)
C(3)—C(4)	1·438 (10)	C(10)—O(11)	1·206 (10)
C(3)—N(1)	1·435 (9)	C(10)—O(12)	1·343 (9)
C(4)—C(5)	1·361 (10)	O(12)—C(13)	1·419 (9)
C(4)—N(7)	1·386 (9)	C(13)—C(14)	1·530 (12)
C(5)—C(6)	1·363 (10)	C(13)—C(15)	1·491 (12)
N(1)—O(1)	1·223 (8)	C(13)—O(22)	1·442 (9)
N(1)—O(2)	1·239 (8)	C(20)—O(21)	1·207 (9)
N(2)—O(3)	1·197 (10)	C(20)—O(22)	1·344 (9)
N(2)—O(4)	1·241 (11)		
C(2)—C(1)—C(6)	122·2 (6)	N(7)—N(8)—C(9)	116·7 (6)
C(6)—C(1)—N(2)	121·1 (8)	N(8)—C(9)—C(10)	127·2 (7)
C(2)—C(1)—N(2)	116·6 (7)	N(8)—C(9)—C(20)	112·1 (6)
C(1)—C(2)—C(3)	118·2 (7)	C(10)—C(9)—C(20)	120·6 (6)
C(2)—C(3)—N(1)	116·5 (7)	C(9)—C(10)—O(11)	123·9 (6)
C(4)—C(3)—N(1)	122·8 (6)	C(9)—C(10) O(12)	115·4 (8)
C(2)—C(3)—C(4)	120·7 (6)	O(11)—C(10)—O(12)	120·5 (7)
C(3)—C(4)—C(5)	117·2 (6)	C(10)—O(12)—C(13)	119·7 (6)
C(3)—C(4)—N(7)	120·7 (6)	O(12)—C(13)—C(14)	106·9 (6)
C(5)—C(4)—N(7)	122·1 (7)	O(12)—C(13)—C(15)	109·8 (7)
C(4)—C(5)—C(6)	122·5 (7)	C(14)—C(13)—C(15)	113·8 (7)
C(1)—C(6)—C(5)	119·1 (7)	O(12)—C(13)—O(22)	109·3 (5)
C(3)—N(1)—O(1)	120·9 (6)	C(14)—C(13)—O(22)	105·6 (7)
C(3)—N(1)—O(2)	117·7 (6)	C(15)—C(13)—O(22)	111·2 (6)
O(1)—N(1)—O(2)	121·4 (6)	C(9)—C(20)—O(21)	125·7 (6)
C(1)—N(2)—O(3)	120·4 (8)	C(9)—C(20)—O(22)	114·5 (6)
C(1)—N(2)—O(4)	115·7 (9)	O(21)—C(20)—O(22)	119·7 (7)
O(1)—N(2)—O(4)	123·8 (9)	C(13)—O(22)—C(20)	120·1 (5)
C(4)—N(7)—N(8)	116·6 (6)		

The dimensions of this hydrogen bond are H(7)···O(1) 2·03 (5), H(7)···O(11) 1·88 (5) Å; N(7)—H(7)···O(1) 119 (4), N(7)—H(7)···O(11) 137 (4)°; the N(7)···O distances are 2·63 (1) and 2·65 (1) Å respectively. These compare to N···O distances of 2·65 and 2·64 Å in (2) and 2·62 and 2·70 Å in dimethyl 2-(2,4-dinitrophenylhydrazono)propanedioate (4). In (2) and (4) the hydrogen atom was not allowed to refine independently and therefore dimensions including H(7) cannot be compared.

Taylor *et al.* (1984) have studied the N—H three-centre bifurcated hydrogen bond from structures in the Cambridge Structural Database (1984). They note that there are 304 examples (only 20% as many as the normal linear two-centre N—H···O hydrogen bond) and of these only 83 have an H···O and H···X distance within 0·2 Å, though this 0·2 Å must clearly be arbitrary given the standard deviations of hydrogen parameters. In (1) the observed 0·15 Å difference may well be within the error limits.

Taylor *et al.* (1984) suggest that the majority of the examples are due to the fortuitous proximity of a proton and an acceptor atom in the same molecule. And this is certainly true of (1) and its analogues.

Furthermore, of the 38 examples with small (<0·1 Å) differences between H···O and H···X distances, most have a considerable difference in N—H···O and N—H···X angles ranging from 0 to 62·4° with an average value of 25·2°.

The present example with very short and also similar H···O distances and N—H···O angles is very rare. Perhaps the only close analogy with two intra-molecular H···O distances close to 2·0 Å and angles close to 120° is 1,2-naphthoquinone 1-(4-chloro-2-nitrophenylhydrazone) (Guggenberger & Teufer, 1975) (H···O 1·825, 1·893 Å, and angles 127·4, 123·5°). It is interesting that in this molecule also the geometry is fixed by other atom positions.
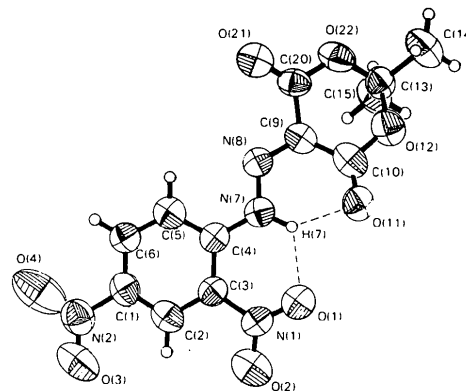

Fig. 1. The structure of (1). 50% probability ellipsoids are shown. For clarity, hydrogen atoms are given a fixed radius.

The dimensions of the phenylhydrazone moiety of (1) are C(4)—N(7) 1·386 (9), N(7)—N(8) 1·330 (8), N(8)—C(9) 1·315 (8) Å. As we have discussed in previous phenylhydrazone structures, the dimensions are dependent primarily on the existence of the α-carbonyl hydrogen bond. Thus with such a bond, mean values for the three bond lengths are 1·400, 1·307, 1·313 Å (18 examples) and without such a bond 1·36, 1·39, 1·28 Å (nine examples). Dimensions in (1) clearly fit in the former category. Another feature of the bifurcated hydrogen bond in this present structure is that angles are enlarged to suit the hydrogen bond. Thus N(8)—C(9)—C(10) is larger than N(8)—C(9)—C(20) by about 15° [viz 127·2 (7) vs 122·1 (6)°]. There is no comparable difference in the angles at C(4) with C(3)—C(4)—N(7), 120·7 (6)°, less than C(5)—C(4)—N(7), 122·1 (7)°.

Least-squares-planes' calculations show that the two nitro groups are closely planar with the phenyl ring intersecting at 5·2 (1) (ortho) and 3·7 (1)° (para). Deviations of atoms from the C(9), C(10), C(20) plane are O(22) 0·15 (1), O(12) 0·12 (1) and C(13) 0·72 (1) Å clearly showing that the dioxane ring is in the envelope formation.

There are no intermolecular distances less than the sum of van der Waals radii.

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Structures of (E)-2,3-Butanedione 2'-Nitrophenylhydrazone (1), C10H11N3O3, (E,E)-2,3-Butanedione Bis(2'-nitrophenylhydrazone) (2), C16H16N6O4, and (E)-2,3-Butanedione 2',4'-Dinitrophenylhydrazone (3), C10H10N4O5

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Abstract. (1) $M_r = 221·22$, orthorhombic, Pmnb, $a = 6·730 (7)$, $b = 11·305 (11)$, $c = 14·160 (15)$ Å, $V = 1077·3$ Å^3, $Z = 4$, $D_x = 1·36$, $D_m = 1·35 (1)$ g cm^{-3}, λ(Mo Kα) = 0·7107 Å, $\mu = 1·11$ cm^{-1}, $F(000) = 464$, room temperature, final $R = 0·061$ for 624 independent observed reflections. The molecule takes up the E conformation so that the carbonyl oxygen is not hydrogen bonded to the NH group. The NH group is, however, hydrogen bonded to the o-nitro group. (2) $M_r = 356·34$, monoclinic, P2$_1$/n, $a = 6·078 (5)$, $b = 5·122 (5)$, $c = 25·800 (7)$ Å, $\beta = 95·6 (1)°$, $V = 799·4$ Å^3, $Z = 2$, $D_x = 1·48$, $D_m = 1·46 (1)$ g cm^{-3}, λ(Mo Kα) = 0·7107 Å, $\mu = 1·19$ cm^{-1}, $F(000) = 372$, room temperature, final $R = 0·091$ for 488 independent observed reflections. The molecule takes up the E,E conformation and contains a crystallographic centre of symmetry. There is a strong intramolecular hydrogen bond between each