

Hydrogen Bonding and Bond Order in Phenylhydrazones: Structures of Diethyl 2-(*o*-Methylphenylhydrazono)-3-oxopentanedioate (1) and Two Forms [One Monoclinic (2*a*), One Orthorhombic (2*b*)] of Diethyl 2-(*p*-Nitrophenylhydrazono)-3-oxopentanedioate

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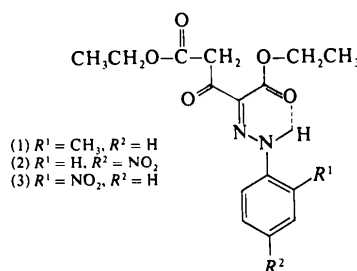
Abstract

Reaction of diethyl 3-oxopentanedioate with substituted benzenediazonium salts in 1:1 ratio gives rise to diethyl 2-(phenylhydrazono)-3-oxopentanedioates. Their IR and ¹H NMR spectra have been discussed in terms of the intramolecular hydrogen bonding between the ester carbonyl and the hydrazone hydrogen. The crystal structures of two of these molecules have been determined. Title compound (1) is triclinic, space group *P*1̄, with *a* = 8.15 (1), *b* = 11.34 (1), *c* = 9.46 (1) Å, α = 102.3 (1), β = 104.5 (1), γ = 95.0 (1)°, *V* = 818.2 Å³, *Z* = 2. Compound (2) crystallizes in two forms; one (2*a*) is monoclinic, space group *P*2₁, with *a* = 4.895 (8), *b* = 12.934 (13), *c* = 13.365 (11) Å, β = 93.6 (1)°, *V* = 844.5 Å³, *Z* = 2 and the other (2*b*) is orthorhombic, space group *P*22₁, with *a* = 4.88 (1), *b* = 13.13 (1), *c* = 26.56 (1) Å, *V* = 1701.8 Å³, *Z* = 4. Data for all three structures were collected on a diffractometer and 1563, 822 and 999 independent intensities above background have been refined to *R* values of 0.074, 0.062 and 0.065 respectively. These structures confirm that there is intramolecular hydrogen bonding between the ester carbonyl and the hydrogen on N(7) of the hydrazone group. The molecular structures of (2*a*) and (2*b*) are identical and the packing is also similar as might be expected from the related unit-cell dimensions. There is no intermolecular hydrogen bond in any of the three structures.

Introduction

The major product isolated from the reaction of diethyl 3-oxopentanedioate (*A*) with an excess of *o*-chlorobenzenediazonium chloride was the bis(phenyl-

hydrazone) derivative diethyl 2,4-bis(*o*-chlorophenylhydrazono)-3-oxopentanedioate (*B*). An X-ray structure analysis shows a dimer molecule with extensive intramolecular hydrogen bonding (Vickery, Willey & Drew, 1981*b*). We now confirm that single coupling occurs on direct 1:1 treatment of (*A*) with the appropriate benzenediazonium salt to give compounds (1)–(3).



The structures of two such derivatives (1) and (2) were investigated to establish that it is the ester (as depicted) rather than the keto-carbonyl group that participates in intramolecular hydrogen bonding and, more generally, to garner further information concerning bond-geometry relationships in phenylhydrazones.

Experimental

IR spectra (Nujol and halocarbon mulls) were recorded on a Perkin–Elmer 580 B spectrophotometer. ¹H NMR spectra (CDCl₃ solutions Me₄Si as reference standard) were obtained using a Bruker WH 90 instrument (90 MHz).

Preparation of compounds

For compound (2) a solution of *p*-nitroaniline (13.8 g) in a 1:1 mixture of concentrated HCl and H₂O

† Deceased.

Table 1. Analytical data

Compound	(1)	(2)	(3)
R ¹	CH ₃	H	NO ₂
R ²	H	NO ₂	H
Formula	C ₁₆ H ₂₀ N ₂ O ₅	C ₁₅ H ₁₇ N ₃ O ₇	C ₁₅ H ₁₇ N ₃ O ₇
m.p. (K)	359–360	382–383	393–394
C _{calc/obs} (%)	60.0/59.6	51.3/51.3	51.3/51.3
H _{calc/obs} (%)	6.3/6.0	4.9/4.8	4.9/4.7
N _{calc/obs} (%)	8.7/8.6	12.0/11.7	12.0/11.8
δ _{NH} (p.p.m.)	13.25	12.94	14.19
δ _{CH₃} (R ¹) (p.p.m.)	2.38		
ν(NH) (cm ⁻¹)	3140	3164	3188

(25/25 cm³) was cooled to 273 K and to it was added a chilled, aqueous solution of sodium nitrite (6.9 g/15 cm³). The resulting solution of *p*-nitrobenzediazonium chloride was filtered rapidly and added, with stirring, to a methanol (50 cm³) solution of diethyl 3-oxopentanedioate (20.2 g) and sodium acetate (17.0 g) maintained at 273 K. After stirring for several hours, the product separated as a dark yellow solid which was recrystallized from ethanol (charcoal) as chunky yellow cuboids m.p. 382–383 K. Analytical data for this and the other compounds are given in Table 1. Compounds (1) and (3) were prepared similarly using the appropriate benzediazonium salt.

Crystal structure determinations

The three crystals were mounted in turn on a Stoe STADI-2 diffractometer and data were collected *via* a variable-width ω scan. Background counts were for 20 s and the scan rate of 0.033° s⁻¹ was applied to a width of (1.5 + sin μ /tan θ). Absorption and extinction corrections were not applied. All three structures were solved by the statistical method. (2a) was solved using *SHELX76* (Sheldrick, 1976) and (1) and (2b) using

Table 2. Additional crystal data and refinement details

	(1)	(2a)	(2b)
M _r	320.2	351.1	351.1
Space group	P $\bar{1}$	P2 ₁	P2 ₂ ,2 ₁
Absences		0k0, k = 2n + 1	0k0, k = 2n + 1 00l, l = 2n + 1
μ (cm ⁻¹)	1.04	1.21	1.21
d _m (g cm ⁻³)	1.32	1.37	1.38
d _c (g cm ⁻³)	1.30	1.38	1.38
λ (Å) for Mo K α	0.7107	0.7107	0.7107
F(000)	340	368	368
Crystal size (mm) [†]	0.3 × 0.5 × 0.5	0.6 × 0.2 × 0.15	0.6 × 0.4 × 0.4
Rotation axis	a	b	c
2 θ maximum (°)	60	50	50
Number of data	3463	1633	1735
Criterion for data inclusion	>2 $\sigma(I)$	>1.5 $\sigma(I)$	>2 $\sigma(I)$
Number of data in refinement	1563	822	999
Number of parameters	265	252	249
R	0.074	0.062	0.065
R _w	0.086	0.065	0.074

[†] These sizes were general for the bulk sample of (2a) and (2b) and we were able to distinguish between the two types visually.

MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Structure (1) could not be solved in space group P $\bar{1}$ and was eventually solved in P1. When all the atoms were located we reverted to the

Table 3. Fractional atomic coordinates (×10⁴) with estimated standard deviations in parentheses for (1)
$$\bar{U} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	\bar{U} (Å ² × 10 ³)
C(1)	2872 (8)	1922 (6)	-3463 (7)	80 (8)
C(2)	3312 (7)	3057 (6)	-3657 (6)	87 (7)
C(3)	4639 (6)	3904 (5)	-2623 (5)	80 (6)
C(4)	5509 (6)	3521 (4)	-1377 (5)	72 (5)
C(5)	5083 (8)	2385 (5)	-1158 (6)	83 (7)
C(6)	3739 (8)	1576 (6)	-2207 (7)	92 (8)
C(7)	5083 (7)	5139 (5)	-2860 (5)	96 (7)
N(7)	6893 (5)	4350 (4)	-336 (4)	71 (5)
N(8)	7753 (5)	4080 (3)	881 (4)	68 (4)
C(9)	9031 (6)	4855 (4)	1858 (5)	69 (5)
C(10)	9559 (6)	6088 (4)	1661 (5)	74 (6)
O(11)	8948 (5)	6411 (3)	522 (4)	93 (4)
O(12)	10719 (4)	6793 (3)	2843 (3)	77 (4)
C(13)	11268 (8)	8007 (5)	2697 (7)	91 (7)
C(14)	12624 (9)	8618 (5)	4118 (7)	104 (9)
C(20)	9924 (7)	4347 (4)	3113 (5)	73 (5)
O(21)	11263 (5)	4851 (3)	3993 (4)	76 (4)
C(22)	9090 (7)	3128 (4)	3229 (5)	76 (6)
C(23)	9556 (9)	2064 (5)	2282 (6)	87 (7)
O(24)	8514 (7)	1216 (5)	1446 (8)	145 (9)
O(25)	11144 (5)	2175 (3)	2321 (4)	91 (5)
C(26)	11733 (12)	1198 (7)	1426 (8)	138 (10)
C(27)	13604 (10)	1339 (7)	2043 (9)	169 (12)

Table 4. Fractional atomic coordinates (×10⁴) for (2a)
$$\bar{U} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	\bar{U} (Å ² × 10 ³)
C(1)	1458 (25)	2621 (13)	6786 (8)	68 (14)
C(2)	3506 (29)	1845 (14)	6779 (8)	85 (16)
C(3)	5058 (24)	1669 (13)	7664 (8)	77 (14)
C(4)	4515 (20)	2230 (12)	8525 (7)	56 (12)
C(5)	2561 (23)	3000	8472 (8)	69 (13)
C(6)	961 (22)	3183 (12)	7614 (8)	68 (13)
N(1)	-207 (28)	2761 (13)	5867 (9)	97 (16)
O(1)	-1755 (22)	3511 (14)	5812 (7)	138 (17)
O(2)	-140 (33)	2166 (14)	5186 (8)	144 (20)
N(7)	5919 (20)	2005 (12)	9436 (7)	63 (11)
N(8)	7838 (19)	1303 (11)	9493 (6)	62 (11)
C(9)	9004 (19)	978 (12)	10370 (7)	57 (11)
C(20)	11163 (21)	190 (12)	10251 (8)	63 (13)
O(21)	12620 (17)	-88 (10)	10960 (6)	96 (11)
C(22)	11675 (19)	-181 (12)	9225 (7)	72 (12)
C(23)	9280 (20)	-791 (13)	8752 (7)	64 (12)
O(24)	7844 (16)	-1322 (12)	9205 (6)	79 (10)
O(25)	9169 (15)	-665 (11)	7767 (5)	79 (9)
C(26)	7011 (29)	-1283 (16)	7206 (9)	76 (18)
C(27)	6884 (45)	-958 (18)	6160 (12)	128 (30)
C(10)	8128 (24)	1395 (14)	11330 (8)	59 (14)
O(11)	6952 (19)	2187 (11)	11391 (6)	100 (11)
O(12)	8846 (19)	799 (11)	12109 (5)	96 (11)
C(13)	8051 (41)	1130 (15)	13099 (10)	122 (21)
C(14)	5820 (42)	621 (20)	13387 (15)	161 (32)

correct space group $P\bar{1}$. The structures were then refined by full-matrix least squares with a weighting scheme that gave similar values for $w\Delta^2$ over ranges of F_o and $\sin \theta/\lambda$. For all three structures, this was $w = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics. O, N and C atoms were refined anisotropically. H atoms bonded to C were placed in tetrahedral or trigonal positions. Their thermal parameters were allowed to refine but those on the same atom were constrained to be equivalent. The H atoms on N(7) were allowed to refine independently. H atoms on methyl groups were refined as rigid groups with a common thermal parameter. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Calculations were made using *SHELX76* on the CDC 7600 computer at the University of Manchester Computer Centre. Additional crystal data and refinement details are given in Table 2. Atomic coordinates are given in Tables 3, 4 and 5. Details of interatomic distances and angles are listed in Table 6.*

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36683 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. Fractional atomic coordinates ($\times 10^4$) for (2b)

	x	y	z	\bar{U} ($\text{\AA}^2 \times 10^3$)
C(1)	2303 (21)	2717 (7)	5866 (3)	71 (11)
C(2)	4316 (24)	1972 (7)	5877 (3)	76 (12)
C(3)	5563 (20)	1754 (6)	6321 (3)	58 (10)
C(4)	4859 (18)	2276 (6)	6759 (3)	58 (9)
C(5)	2803 (20)	3018 (6)	6736 (3)	62 (10)
C(6)	1492 (20)	3231 (7)	6292 (3)	69 (11)
N(7)	5992 (18)	2044 (5)	7219 (3)	61 (9)
N(8)	7877 (15)	1323 (5)	7261 (3)	55 (8)
C(9)	8843 (19)	1005 (6)	7686 (3)	61 (9)
C(10)	7835 (20)	1413 (7)	8177 (3)	64 (10)
O(11)	6640 (18)	2197 (5)	8202 (2)	79 (9)
O(12)	8424 (17)	810 (5)	8555 (2)	79 (9)
C(13)	7529 (40)	1151 (11)	9064 (4)	113 (20)
C(14)	5193 (41)	596 (15)	9213 (7)	141 (33)
C(20)	11115 (20)	224 (6)	7631 (3)	67 (10)
O(21)	12361 (18)	-84 (6)	7991 (3)	94 (10)
C(22)	11723 (18)	-132 (7)	7106 (3)	65 (10)
C(23)	9544 (16)	-755 (7)	6871 (3)	46 (10)
O(24)	8071 (16)	-1311 (5)	7103 (2)	78 (8)
O(25)	9516 (13)	-647 (5)	6379 (2)	78 (7)
C(26)	7491 (31)	-1305 (10)	6101 (4)	136 (18)
C(27)	7024 (44)	-886 (12)	5631 (5)	159 (23)
N(1)	913 (25)	2939 (8)	5389 (3)	100 (13)
O(1)	-761 (24)	3627 (8)	5370 (3)	126 (14)
O(2)	1552 (24)	2415 (7)	5031 (3)	133 (14)

Discussion

An intense absorption band $\nu(\text{NH})$ in the region 3140–3188 cm^{-1} and the low-field δ_{NH} 12.94–14.19

Table 6. Molecular dimensions (\AA and deg)

	(1)	(2a)	(2b)
C(1)–C(2)	1.370 (9)	1.387 (13)	1.419 (17)
C(1)–C(6)	1.376 (9)	1.374 (12)	1.359 (15)
C(2)–C(3)	1.393 (7)	1.357 (12)	1.384 (14)
C(3)–C(4)	1.390 (6)	1.393 (10)	1.399 (14)
C(3)–C(7)	1.494 (7)		
C(4)–C(5)	1.378 (7)	1.400 (12)	1.391 (12)
C(4)–N(7)	1.412 (6)	1.375 (10)	1.380 (15)
C(5)–C(6)	1.386 (8)	1.371 (12)	1.368 (14)
C(1)–N(1)		1.467 (12)	1.467 (12)
N(1)–O(1)		1.219 (12)	1.230 (15)
N(1)–O(2)		1.214 (10)	1.194 (14)
N(7)–N(8)	1.302 (5)	1.325 (9)	1.305 (12)
N(8)–C(9)	1.313 (5)	1.292 (10)	1.339 (11)
C(9)–C(10)	1.492 (6)	1.492 (12)	1.481 (15)
C(9)–C(20)	1.484 (6)	1.517 (12)	1.483 (14)
C(10)–O(11)	1.213 (5)	1.186 (10)	1.181 (14)
C(10)–O(12)	1.321 (5)	1.310 (10)	1.324 (13)
O(12)–C(13)	1.456 (6)	1.489 (12)	1.466 (14)
C(13)–C(14)	1.495 (8)	1.409 (22)	1.352 (21)
C(20)–O(21)	1.203 (5)	1.205 (10)	1.204 (11)
C(20)–C(22)	1.525 (7)	1.499 (12)	1.490 (14)
C(22)–C(23)	1.480 (8)	1.481 (11)	1.517 (14)
C(23)–O(24)	1.213 (7)	1.195 (9)	1.178 (11)
C(23)–O(25)	1.280 (7)	1.315 (9)	1.323 (11)
O(25)–C(26)	1.439 (8)	1.505 (12)	1.489 (14)
C(26)–C(27)	1.471 (10)	1.384 (14)	1.458 (20)
C(2)–C(1)–C(6)	120.4 (5)	122.3 (8)	123.1 (9)
C(2)–C(1)–N(1)		119.1 (9)	116.4 (12)
C(6)–C(1)–N(1)		118.6 (10)	120.4 (12)
C(1)–C(2)–C(3)	122.5 (5)	118.9 (8)	117.4 (10)
C(2)–C(3)–C(4)	115.8 (5)	120.8 (8)	119.6 (10)
C(4)–C(3)–C(7)	122.9 (4)		
C(2)–C(3)–C(7)	121.3 (4)		
C(5)–C(4)–C(3)	122.6 (4)	118.9 (8)	120.0 (10)
C(5)–C(4)–N(7)	120.6 (4)	122.3 (7)	119.9 (9)
C(3)–C(4)–N(7)	116.8 (4)	118.8 (7)	120.1 (10)
C(4)–C(5)–C(6)	119.7 (5)	120.9 (8)	121.8 (10)
C(1)–C(6)–C(5)	118.9 (6)	118.2 (8)	117.9 (10)
C(4)–N(7)–N(8)	121.0 (4)	120.9 (7)	120.7 (9)
N(7)–N(8)–C(9)	121.1 (4)	124.0 (7)	122.4 (9)
N(8)–C(9)–C(10)	122.6 (4)	121.8 (8)	120.9 (10)
N(8)–C(9)–C(20)	112.9 (4)	113.6 (7)	113.0 (8)
C(10)–C(9)–C(20)	124.4 (4)	124.6 (8)	126.1 (9)
C(9)–C(10)–O(11)	122.6 (4)	121.6 (8)	123.0 (11)
C(9)–C(10)–O(12)	113.8 (3)	112.4 (8)	113.1 (11)
O(11)–C(10)–O(12)	123.6 (4)	126.0 (8)	123.8 (11)
C(10)–O(12)–C(13)	115.5 (3)	116.7 (8)	117.9 (10)
O(12)–C(13)–C(14)	106.5 (4)	109.7 (13)	112.3 (15)
C(9)–C(20)–O(21)	122.3 (8)	121.3 (8)	120.8 (9)
C(9)–C(20)–C(22)	117.1 (4)	116.4 (7)	118.8 (9)
O(21)–C(20)–C(22)	120.6 (4)	122.3 (8)	120.1 (10)
C(20)–C(22)–C(23)	113.3 (4)	115.0 (7)	112.4 (7)
C(22)–C(23)–O(24)	123.4 (6)	123.5 (7)	124.0 (9)
C(22)–C(23)–O(25)	113.5 (4)	111.6 (7)	109.4 (9)
O(24)–C(23)–O(25)	122.7 (6)	124.9 (7)	126.5 (9)
C(23)–O(25)–C(26)	118.2 (5)	115.6 (7)	114.7 (9)
O(25)–C(26)–C(27)	107.1 (5)	108.8 (10)	108.3 (12)
C(1)–N(1)–O(1)		119.5 (10)	117.6 (12)
C(1)–N(1)–O(2)		116.4 (11)	121.8 (14)
O(1)–N(1)–O(2)		124.1 (10)	120.6 (13)

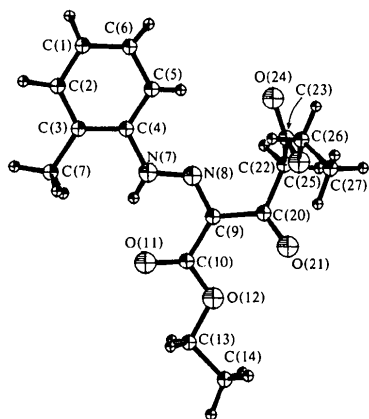


Fig. 1. Molecule (1) with atom numbering.

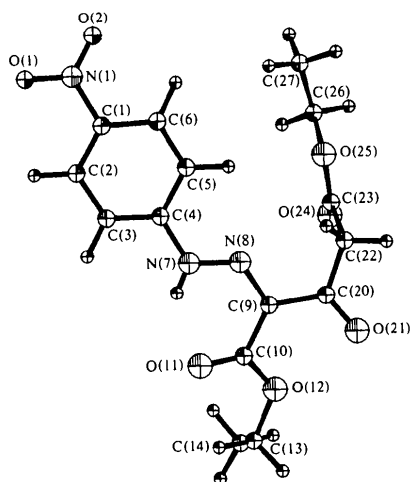


Fig. 2. Molecule (2a) with atom numbering.

p.p.m. (Table 1) clearly establish the presence of hydrogen bonding. Variations in δ_{NH} follow the expected trend *o*-nitro > *o*-methyl > *p*-nitro though the magnitude of the downfield shift for (1) with an ostensibly non-participating *o*-methyl group is greater, perhaps, than might have been anticipated.

We prepared (2) as described above and recrystallized it from ethanol. We found from precession photographs that there were two types of crystal in the sample. They were found to have related cell dimensions with volumes in the ratio 1:2 and different space groups. We decided to solve both structures to investigate why compound (2) crystallized in two ways. We found that (2a) and (2b) had identical molecules but there were some small variations in the packing in the two space groups. These intermolecular effects are discussed later. The molecular structures will be considered first. Those of (1) and (2a) are shown in Figs. 1 and 2 together with their atom numbering. The structure of (2b) is identical with that of (2a) and is

therefore not shown. In all three it is the ester carbonyl [*viz* O(11)] that participates in hydrogen bonding with N(7); distances for N(7)···O(11) are 2.60, 2.64, 2.64 Å in (1), (2a) and (2b) respectively.

As we have reported previously (Kaberia, Vickery, Willey & Drew, 1980; Vickery, Willey & Drew, 1981a, c) phenylhydrazones which have terminal C=O groups conjugating to the N(8)=C(9) bonds exhibit particular dimensions in the C(4)–N(7)–N(8)=C(9) moiety. We averaged data for eight compounds and found mean values of C(4)–N(7) 1.41, N(7)–N(8) 1.34 and N(8)–C(9) 1.31 Å. These were respectively +0.05, –0.05 and +0.03 Å different from those without such a terminal –C=O group. In the present series of molecules these trends are followed for the most part. In (1) the values are 1.412 (6), 1.302 (5), 1.313 (5) Å but in (2a) and (2b) C(4)–N(7) is shorter at 1.375 (10), 1.380 (15) although N(7)–N(8) at 1.325 (9), 1.305 (12) and N(8)–C(9) at 1.292 (10), 1.339 (11) Å are comparable with the mean values. Of course (1) and (2) have different substituent groups on the phenyl rings and it is interesting to consider whether they make any difference to the hydrazone dimensions. In (4) of Vickery *et al.* (1981a), the presence of a *p*-nitro group

Table 7. Least-squares planes for (1), (2a) and (2b)

Distances of atoms (Å) from the plane of atoms C(*n*), *n* = 1...6, are given. Standard deviations of atoms from the planes are 0.01 Å.

	(1)	(2a)	(2b)
C(1)	0.00	0.00	0.01
C(2)	0.00	0.00	0.00
C(3)	–0.01	0.01	–0.01
C(4)	0.00	–0.02	0.01
C(5)	0.00	0.02	0.01
C(6)	–0.01	0.02	0.01
N(1)		–0.07	0.00
O(1)		0.09	0.07
O(2)		–0.30	–0.07
C(7)	–0.02		
N(7)	0.04	–0.12	–0.06
N(8)	0.02	–0.11	–0.11
C(9)	0.03	–0.36	–0.29
C(10)	0.06	–0.67	–0.52
C(20)	0.10	–0.29	–0.21

Angle of intersection (°) between the above phenyl-ring plane and the following planes (which are all planar within experimental error) with e.s.d.'s in parentheses

	(1)	(2a)	(2b)
(B) C(9), C(10), O(11), O(12)	7.2 (2)	27.6 (3)	24.6 (4)
Deviations from plane (B) (Å)			
C(13)	0.00	0.00	0.00
C(14)	0.05	–1.23	–1.27
(C) C(9), C(20), O(21), C(22)	10.2 (2)	8.5 (2)	5.8 (2)
(D) C(22), C(23), O(24), O(25)			
Angles between planes (C) and (D)	78.4 (3)	80.5 (4)	86.9 (7)
Deviations from plane (D) (Å)			
C(26)	0.01	–0.08	–0.09
C(27)	0.41	–0.09	0.35

in dimethyl 2-(2,4-dinitrophenylhydrazono)propanedioate is also concomitant with a shorter N(7)—N(8) distance namely 1.280 (12) Å. There are not enough examples to say whether this is a significant trend but all three molecules with *p*-nitro groups have an N—N bond length shorter than the norm.

In (1) there is an *o*-methyl group C(7) and, as can be seen from Fig. 1, the C(4)—C(3)—C(7)—H torsion angles of 64.4, -53.1 and -174.1° ensure that the H atoms are arranged around the C(3)—C(7) bond so that they are as far away from N(7) and H(7) as possible. The presence of the methyl group has very little effect on the geometry of the molecule. C(7) is coplanar with the phenyl ring and the C(7)—C(3)—C(4)—N(7) torsion angle is only -1.7°. Indeed the whole molecule is more planar than (2*a*) and (2*b*) which contain a *p*-nitro group and no *ortho* group. As can be seen from the least-squares-plane calculations in Table 7 the maximum distance of any of the five atoms N(7), N(8), C(9), C(10) and C(20) from this phenyl-ring plane is 0.10 Å. In (2*a*) and (2*b*), the value is over 0.50 Å and it seems that the planarity of the hydrazone group with the benzene ring is directly related to the nature of the *ortho* group.

Table 8. Intermolecular distances less than 3.50 Å in (1), (2*a*) and (2*b*)

In (1)			
C(20)...O(21 ^h)	3.11 (1)	N(8)...O(11 ^h)	3.21 (1)
O(21)...C(22 ^h)	3.19 (1)	O(11)...C(9 ^h)	3.28 (1)
O(21)...O(21 ^h)	3.13 (1)	C(26)...O(24 ^h)	3.37 (1)
O(21)...C(7 ^h)	3.41 (1)	C(10)...C(2 ^h)	3.44 (1)
C(10)...N(7 ^h)	3.46 (1)	N(8)...C(7 ^h)	3.38 (1)
O(25)...C(11 ^h)	3.40 (1)		
In (2 <i>a</i>)			
C(3)...C(6 ^v)	3.50 (2)	C(5)...O(24 ^h)	3.24 (1)
C(22)...O(24 ^v)	3.36 (1)	O(11)...O(24 ^h)	3.10 (1)
C(2)...O(1 ^v)	3.47 (2)	O(11)...C(26 ^h)	3.41 (2)
O(21)...C(10 ^v)	3.32 (2)	C(6)...O(12 ^h)	3.40 (2)
C(5)...O(21 ^h)	3.47 (1)	N(7)...O(24 ^h)	3.43 (2)
O(11)...O(24 ^h)	3.33 (2)	O(2)...C(27 ^h)	3.47 (3)
O(11)...C(23 ^v)	3.21 (2)	C(13)...O(2 ^h)	3.17 (2)
C(6)...O(21 ^h)	3.48 (2)		
In (2 <i>b</i>)			
C(3)...C(6 ^v)	3.48 (1)	C(6)...O(21 ^h)	3.47 (1)
C(22)...O(24 ^v)	3.46 (1)	C(5)...O(24 ^h)	3.24 (1)
C(2)...O(1 ^v)	3.51 (1)	O(11)...O(24 ^h)	3.13 (1)
O(21)...C(10 ^v)	3.35 (1)	O(11)...C(26 ^h)	3.37 (1)
C(5)...O(21 ^h)	3.51 (1)	C(6)...O(12 ^h)	3.41 (1)
O(11)...O(24 ^h)	3.34 (1)	C(13)...O(2 ^h)	3.22 (1)
O(11)...C(23 ^v)	3.28 (1)	C(27)...O(2 ^h)	3.46 (1)
Symmetry code			
None	x, y, z	(vii)	$1 - x, \frac{1}{2} + y, 2 - z$
(i)	$2 - x, 1 - y, 1 - z$	(viii)	$1 - x, \frac{1}{2} + y, 1 - z$
(ii)	$2 - x, 1 - y, -z$	(ix)	$1 + x, y, 1 + z$
(iii)	$2 - x, -y, -z$	(x)	$2 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$
(iv)	$1 - x, 1 - y, -z$	(xi)	$1 - x, \frac{1}{2} + y, 1\frac{1}{2} - z$
(v)	$1 + x, y, z$	(xii)	$1 - x, \frac{1}{2} - y, -\frac{1}{2} + z$
(vi)	$2 - x, \frac{1}{2} + y, 2 - z$	(xiii)	$1 + x, -y, 1 - z$

Three categories are apparent. (i) When there is an *o*-chloro group as in (2*a*) and (2*b*) of Vickery *et al.* (1981*b*) or a methyl group as in (1) in the present case then the hydrazone group is almost coplanar with the phenyl ring. It is strange that the effects of the two atoms should be the same. It is clear why the methyl group should cause this planarity because of the need to maximize H...H interactions. But one might expect a chlorine to have a different effect. In diethyl 2,4-bis(*o*-chlorophenylhydrazono)-3-oxopentanedioate deviations are only up to 0.25 Å despite the structural complexities introduced by the dimer form. (ii) The second category with slightly larger deviations consists of molecules where there is an *o*-nitro group which is hydrogen bonded to H(7). Both (1) of Vickery *et al.* (1981*b*) and (4) of Vickery *et al.* (1981*a*) are examples in this category. (iii) The final category includes those compounds where there are no *ortho* groups present as, for example, in (2*a*) and (2*b*) in the present instance and in (3) in Vickery *et al.* (1981*a*). These have the largest deviations presumably because steric effects are at a minimum and the molecule can adjust to intra- and intermolecular packing effects.

The geometry of the remainder of the molecules is straightforward. The ester carbonyl participates in hydrogen bonding as we have seen and this grouping remains relatively planar with the phenyl ring. The C(9), C(10), O(11), O(12) plane intersects that ring at 7.2° in (1), and at 27.6 and 24.6° in (2*a*) and (2*b*) respectively. C(13) is coplanar with those four atoms but C(14) can of course rotate around the O(12)—C(13) bond. In (1) the C(10)—O(12)—C(13)—C(14) torsion angle is -177.4° while in (2*a*) and (2*b*) it is 100.6 and 103.8° respectively. Clearly the difference must be due to packing effects as there can be only a marginal difference in intramolecular strain. The atoms C(9), C(20), O(21) and C(22) are also close to the phenyl-ring plane intersecting at 10.2, 8.5 and 5.8° respectively for (1), (2*a*) and (2*b*). The C(9)—C(20)—C(22)—C(23) torsion angles are 85.5, -66.8 and -67.7° respectively for (1), (2*a*) and (2*b*). A further plane is formed by atoms C(22), C(23), O(24) and O(25). These latter two planes (named *C* and *D* in Table 7) are then almost perpendicular to each other in all three structures. C(27) is almost coplanar in all three structures with the acetyl group with C(23)—O(25)—C(26)—C(27) torsion angles of -160.9, 172.1 and -160.9° for (1), (2*a*) and (2*b*) respectively.

In Table 8, we list the intermolecular contacts less than 3.50 Å. There are similar numbers in all three crystal structures indicating reasonably efficient packing. The unit cell of (1) is unremarkable. The major points of interest in (2*a*) and (2*b*) are the related cell dimensions. (2*a*) crystallizes in monoclinic space group *P*2₁ and (2*b*) in orthorhombic space group *P*2₂, 2₁. The only significant change in the size of the two unit cells is the doubling of the *c* axis (13.365 and 26.56 Å

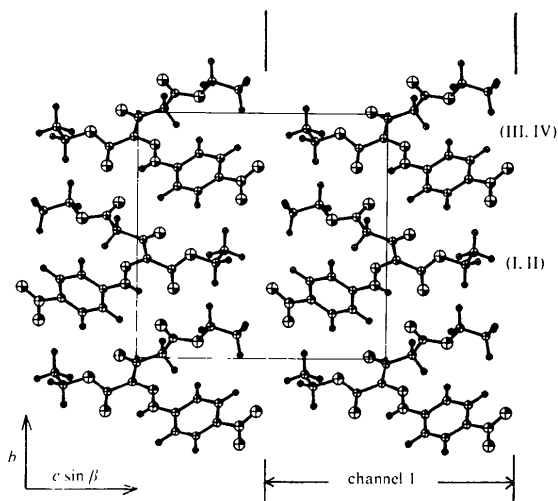


Fig. 3. The unit cell of (2a) in the a projection.

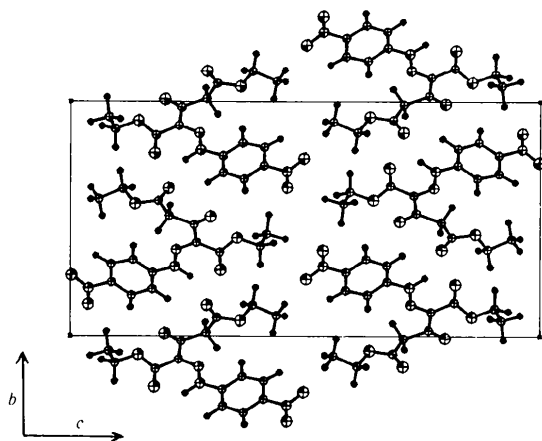


Fig. 4. The unit cell of (2b) in the a projection.

respectively). We have chosen the y coordinates in (2a) to match those in (2b) and show in Figs. 3 and 4 the two unit cells in the a projection, down the 4.9 \AA axis. As can be seen the molecules are packed along the y axis in identical fashion. The intermolecular contacts show that the closest contacts in (2a) are between the x, y, z molecules (I) and the molecules at $1 + x, y, z$ (II), $2 - x, \frac{1}{2} + y, 2 - z$ (III) and $1 - x, \frac{1}{2} + y, 2 - z$ (IV).

These contacts are solely between the molecules in the x and y directions (*i.e.* in channel 1 of Fig. 3) and do not involve translation in z . There is just one close contact that does involve such a translation in z , namely $C(13) \cdots O(2)(1 + x, y, 1 + z)$ of 3.17 \AA . This pattern is exactly maintained in (2b). Indeed the close contacts are identical as can be seen from Table 8 and clearly there is close packing along x and y but not along z . The inability of the molecules to pack efficiently along z gives rise to the two crystal forms presumably of equivalent packing energy. In (2a) the repeat distance in z takes in one molecule. In (2b), there are two such molecules related by the symmetry element $-x, \frac{1}{2} - y, \frac{1}{2} + z$. Thus in (2a), the pattern is *AAAAA* and in (2b) *ABABABAB*. There is no significant difference either in the density or in the efficiency of the packing as measured by the non-bonded contacts involving translation along z . There is no intermolecular hydrogen bonding in any of the three structures.

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