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

By Gerald R. Willey

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

and Michael G. B. Drew

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, England

Abstract. (1) $M_r = 221 \cdot 22$, orthorhombic, $Pmnb$, $a = 6 \cdot 730$ (7), $b = 11 \cdot 305$ (11), $c = 14 \cdot 160$ (15) Å, $V = 1077 \cdot 3$ Å³, $Z = 4$, $D_x = 1 \cdot 36$, $D_m = 1 \cdot 35$ (1) g cm⁻³, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1 \cdot 11$ cm⁻¹, $F(000) = 464$, room temperature, final $R = 0 \cdot 061$ 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) $M_r = 356 \cdot 34$, monoclinic, $P2_1/n$, $a = 6 \cdot 078$ (5), $b = 5 \cdot 122$ (5), $c = 25 \cdot 800$ (7) Å, $\beta = 95 \cdot 6$ (1)°, $V = 799 \cdot 4$ Å³, $Z = 2$, $D_x = 1 \cdot 48$, $D_m = 1 \cdot 46$ (1) g cm⁻³, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1 \cdot 19$ cm⁻¹, $F(000) = 372$, room temperature, final $R = 0 \cdot 091$ 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

NH group and the corresponding *o*-nitro group. (3) $M_r = 266·21$, monoclinic, $P2_1/c$, $a = 10·013$ (9), $b = 11·630$ (11), $c = 10·529$ (12) Å, $\beta = 108·0$ (1)°, $V = 1166·2$ Å^3, $Z = 4$, $D_x = 1·51$, $D_m = 1·49$ (1) g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 1·34$ cm^{-1}, $F(000) = 552$, room temperature, final $R = 0·065$ for 1377 independent observed reflections. The molecule, like (1), rather surprisingly takes up the E conformation so that the carbonyl oxygen is not hydrogen bonded.

Introduction. In a recent report (Willey & Drew, 1983), one in a series from these laboratories covering spectral and structural parameters of various phenylhydrazone derivatives (Kaberia, Vickery, Willey & Drew, 1980; Vickery, Willey & Drew, 1981*a,b*; Drew, Vickery & Willey 1982*a*), the structures of the mono- and bis(*p*-nitrophenylhydrazone) derivatives of 2,3-butanedione (compounds 5 and 6 respectively) are described. One of the intriguing aspects of the mono-compound is that rather than the expected Z isomer with incipient N—H···O=C intramolecular hydrogen bonding, it is the E isomer that is formed with accompanying intermolecular chains of hydrogen bonds. Conjecture as to whether the introduction of an *o*-NO$_2$ group on the aromatic ring would reverse this tendency and lead to the Z isomer was mentioned at the time. As for the bis-derivative, which has the E,E conformation, the inclusion of a molecule of dimethylformamide (DMF) strongly hydrogen bonded to each NH centre brings into question the criticality of the solvent with respect to the particular structure ultimately adopted.

The phenylhydrazone derivatives of 2,3-butanedione under scrutiny, (1)–(4), form a suitable reference set to evaluate these several points and also to extend the available structural data concerning N—H···X (X = —CO, NO$_2$) hydrogen bonding which is now a recognized feature of such derivatives.
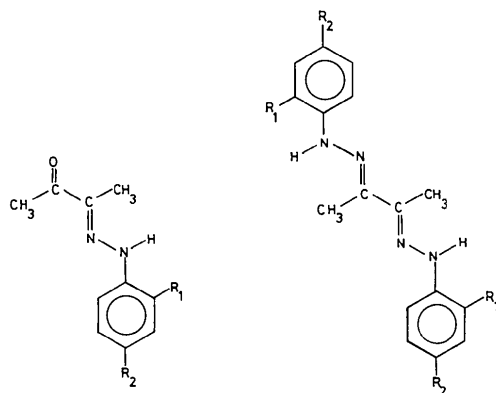
The four phenylhydrazone derivatives of 2,3-butanedione (1)–(4) were prepared *via* condensation reactions of the dione and the appropriate phenylhydrazine under suitably controlled conditions.

2,3-Butanedione 2'-nitrophenylhydrazone (1). A solution of *o*-nitrophenylhydrazine (6·1 g, 0·04 mol) in ethanol (100 cm^3) containing several drops of glacial acetic acid was added to 2,3-butanedione (3·4 g, 0·04 mol) and the mixture was stirred for 2 h at 273 K. After standing for 10 min the resulting orange solid was collected by filtration and suspended in ethanol (2 ×30 cm^3) to remove any unchanged reactants and finally washed with dichloromethane (3 × 30 cm^3). Recrystallization from boiling dichloromethane/ petroleum ether (313–333 K) gave orange needle crystals (1·4 g, yield 16%).

2,3-Butanedione bis(2'-nitrophenylhydrazone) (2). A mixture of *o*-nitrophenylhydrazine (9·2 g, 0·06 mol), several drops of glacial acetic acid and 2,3-butanedione (1·72 g, 0·02 mol) in ethanol (75 cm^3) was heated at reflux for 6 h. Filtration of the resulting mixture gave a red precipitate which was suspended in boiling ethanol (30 cm^3) for 5 min to remove any impurities. The red product was collected by filtration and recrystallized from boiling DMF to give deep-red-brown fibrous needle crystals (3·6 g, yield 25%).

The dinitro derivatives (3) and (4) were similarly prepared using 2,4-dinitrophenylhydrazine under the appropriate conditions. For analytical and spectral characterization, see Table 1.

Suitable crystals of (1), (2) and (3) selected from recrystallized samples obtained as described above and placed in Lindemann tubes. Densities measured by flotation. Precession photographs established preliminary cell constants and space groups. Crystals, approximate sizes 0·1 × 0·5 × 0·1 (1), 0·2 × 0·3 × 0·3 (2), 0·4 × 0·4 × 0·4 mm (3), mounted on a Stoe STADI2 diffractometer to rotate about the a, b and a axes respectively. Cell dimensions obtained by measurement of *ca* 20 high-angle axial reflections. Space groups from systematic absences $hk0$, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$ (1), $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$ (2), $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$ (3). Intensity data collected *via* variable-width ω scan, background counts 20s, step-scan rate of 0·033° s^{-1} applied to a width of $(1·5 + \sin\mu/\tan\theta)°$. Absorption and extinction correc-

(1) R$_1$ = NO$_2$ R$_2$ = H
(3) R$_1$ = NO$_2$ R$_2$ = NO$_2$
(5) R$_1$ = H   R$_2$ = NO$_2$

(2) R$_1$ = NO$_2$ R$_2$ = H
(4) R$_1$ = NO$_2$ R$_2$ = NO$_2$
(6) R$_1$ = H   R$_2$ = NO$_2$

Table 1. *Microanalytical and spectral data for phenylhydrazone derivatives*

| Com-pound | Formula | Colour | M_r | M.p. (K) | Microanalyses (%) calculated/observed | | | Mass spectral (M^+/z) | $\nu(NH)^*$ | δ_{NH}† | δ_{CH_3}† | Electronic‡ (λ_{max}) |
					C	H	N					
(1)	$C_{10}H_{11}N_3O_3$	Orange	221·22	443–444	54·3/54·0	5·0/4·9	19·0/18·8	221	3326	10·95	2·08 2·50	23 980 (10 000) 25 252 (9 600) 32 258 (19 300)
(2)	$C_{16}H_{16}N_6O_4$	Red-brown	356·34	577–578	53·9/53·9	4·5/4·5	23·6/23·6	356	3319	10·94	2·09 2·50	21 008 (16 200) 29 670 (sh) 30 120 (24 400)
(3)	$C_{10}H_{10}N_4O_5$	Tangerine	266·21	448–449	45·1/45·1	3·8/3·8	21·0/21·1	266	3305	11·15	2·17 2·53	25 316 (sh) 27 548 (23 200)
(4)	$C_{16}H_{14}N_8O_8$	Brown-red	446·34	598–599 (decomp.)	43·1/42·9	3·2/3·1	25·0/24·6	446	3300	—	—	22 727 (sh) 25 316 (38 300)

* (cm^{-1}) Nujol mull.
† In $CDCl_3$ solutions with respect to tetramethylsilane $(\delta = 0)$.
‡ (cm^{-1}) in CH_2Cl_2 solutions $(1 \times 10^{-4}M)$ with ε_{max} in parentheses.

tions not applied. Standard reflections $h22$ (1), $2k2$ (2) and $h22$ (3) measured every 20 measurements for each layer; no significant change in intensity. 1092 $(0 < h < 7, 0 < k < 13, 0 < l < 15)$, 1419 $(0 < h < 7, 0 < k < 5, -32 < l < 26)$, 2063 $(0 < h < 11, 0 < k < 12, -15 < l < 10)$ data measured with $2\theta_{max}$ of 50°. 624, 488, 1377 independent data with $I > 2\sigma(I)$, $2\sigma(I)$, $3\sigma(I)$ refined (on F) to R 0·061, 0·091, 0·065 respectively $(wR$ 0·066, 0·096, 0·065; S 2·32, 2·54, 1·88). Weighting schemes chosen to give similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F_o; for all three structures, $w = 1/[\sigma^2(F) + 0·03F^2]$, $\sigma(F)$ from counting statistics. All three structures solved using *MULTAN*80 (Main *et al.*, 1980). Hydrogen atoms bonded to carbon included in calculated positions and their thermal parameters refined. Hydrogen atoms on the same carbon atom given an equivalent thermal parameter. H(7) bonded to N(7) was allowed to refine independently. Non-hydrogen atoms refined anisotropically *via* full-matrix least squares.

There was some ambiguity as to the space group of (1) which could be $P2_1nb$ or $Pmnb$. In the latter space group the molecule has crystallographically imposed C_s symmetry. The structure was refined in both space groups and R values of 0·0585 (160 variables) and 0·0610 (119 variables) were obtained. We have adopted the structure in the centrosymmetric space group primarily because the structure obtained from the $P2_1nb$ had some unlikely features including a benzene ring which was signficantly non-planar. The structure of (2) contains a crystallographic centre of symmetry but no signs of disorder. The refinement of (3) was straightforward.

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 >0·1σ. Calculations carried out using *SHELX*76 (Sheldrick, 1976) at the University of Manchester Computer Centre.

Discussion. Final coordinates are given in Tables 2, 3 and 4. Molecular dimensions are compared in Table 5.*

The four phenylhydrazone derivatives of 2,3-butanedione (1)–(4) featuring both o- and p-nitro-group substituents on the aromatic ring have been isolated *via* controlled condensation reactions of the dione and the appropriate phenylhydrazine. Simple 1:1 addition in the presence of a few drops of glacial acetic acid followed by stirring for 2 h suffices for the mono-derivatives; for the bis-derivatives an excess (two to threefold) of phenylhydrazine and much more belligerent reaction conditions are necessary. We have utilized this differential approach for a variety of diones previously (Drew, Vickery & Willey, 1981, 1982b; Willey & Drew, 1983).

Microanalytical and spectral data are listed in Table 1. The mono-derivatives (1) and (3) were quite soluble in the common organic solvents and crystallization was straightforward from dichloromethane solutions; both gave needle crystals. The bis-derivatives proved the opposite, *e.g.* brown-red fibrous needles of (2) were finally obtained with great difficulty from DMF solutions. Because of the limited solubility of (4) we were unable to obtain reliable ^1H NMR data (or for that matter crystals) but by analogy with (2) it can be assumed that the E,E isomer is formed.

From previous ^1H NMR studies we have shown that variations in δ_{NH} can be reliably correlated with the extent and type of hydrogen bonding present, *e.g.* (*a*) NH_{free} $\delta7$–9; (*b*) $NH_{solvent}$ $\delta9$–11; (*c*) NH_{intra} (either from an adjacent α-oxo group or an o-NO_2 substituent on the aromatic ring) $\delta10$–13; (*d*) $NH_{bifurcated}$ (both α-oxo group and o-NO_2 substituent) $\delta13$–15. The series (1)–(3) shows one resonance in the range δ_{NH} 10·94–11·15, *viz* type (*c*) which is in accord with the presence

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for* (1) *with e.s.d's in parentheses*

	x	y	z	$\bar{U}_{eq}{}^*(\text{Å}^2)$
C(1)	7500	6974 (5)	−1172 (4)	72 (4)
C(2)	7500	7074 (5)	−212 (4)	67 (4)
C(3)	7500	6064 (4)	354 (4)	56 (4)
C(4)	7500	4927 (5)	−42 (4)	57 (4)
C(5)	7500	4856 (4)	−1030 (3)	63 (4)
C(6)	7500	5860 (5)	−1573 (4)	65 (4)
N(7)	7500	3924 (3)	492 (3)	60 (3)
N(8)	7500	2869 (3)	70 (3)	59 (3)
C(9)	7500	1945 (4)	591 (4)	64 (4)
C(20)	7500	812 (5)	67 (5)	87 (5)
O(21)	7500	−94 (4)	521 (4)	113 (5)
C(10)	7500	1925 (4)	1644 (5)	85 (5)
C(22)	7500	822 (7)	−975 (6)	96 (7)
N(1)	7500	6244 (4)	1353 (3)	77 (4)
O(1)	7500	5424 (4)	1904 (3)	91 (4)
O(2)	7500	7250 (4)	1644 (4)	157 (6)

$$* \ \bar{U}_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$) *for* (2) *with e.s.d.'s in parentheses*

	x	y	z	$\bar{U}_{eq}{}^*(\text{Å}^2)$
C(1)	4278 (23)	4605 (24)	2877 (5)	67 (16)
C(2)	5702 (21)	2624 (24)	3050 (4)	58 (16)
C(3)	5281 (20)	1097 (22)	3486 (5)	49 (14)
C(4)	3425 (19)	1579 (22)	3763 (5)	49 (13)
C(5)	2055 (19)	3682 (22)	3574 (5)	51 (15)
C(6)	2497 (21)	5092 (25)	3148 (5)	72 (16)
N(7)	2949 (19)	247 (21)	4177 (4)	61 (13)
N(8)	1239 (17)	957 (18)	4455 (4)	57 (12)
C(9)	917 (18)	−416 (20)	4856 (4)	34 (12)
N(1)	6873 (19)	−950 (20)	3626 (4)	61 (13)
O(1)	6564 (15)	−2267 (16)	4018 (3)	76 (11)
O(2)	8396 (14)	−1300 (19)	3365 (4)	92 (13)
C(10)	2307 (20)	−2756 (23)	5036 (5)	60 (15)

$$* \ \bar{U}_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

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

	x	y	z	$\bar{U}_{eq}{}^*(\text{Å}^2)$
C(1)	1168 (3)	6280 (3)	−838 (3)	66 (3)
C(2)	1933 (3)	6613 (3)	446 (3)	62 (3)
C(3)	2530 (3)	5803 (3)	1409 (3)	58 (3)
C(4)	2369 (3)	4599 (3)	1110 (3)	60 (3)
C(5)	1563 (3)	4302 (3)	−222 (3)	62 (3)
C(6)	969 (3)	5115 (3)	−1181 (3)	61 (3)
C(9)	3435 (3)	1923 (3)	2633 (3)	69 (3)
C(20)	3293 (4)	683 (3)	2207 (4)	83 (4)
O(21)	4048 (3)	−23 (3)	2960 (3)	112 (4)
N(2)	543 (3)	7154 (3)	−1856 (3)	72 (3)
N(1)	3345 (3)	6225 (3)	2748 (3)	63 (3)
N(7)	2950 (3)	3779 (2)	2052 (3)	63 (3)
N(8)	2775 (3)	2648 (2)	1703 (3)	66 (3)
O(3)	682 (3)	8164 (3)	−1535 (3)	94 (3)
O(4)	−107 (3)	6830 (3)	−3001 (3)	93 (4)
O(2)	3483 (3)	7258 (2)	2913 (3)	78 (3)
O(1)	3848 (3)	5541 (2)	3664 (3)	81 (3)
C(10)	4343 (4)	2224 (3)	4039 (4)	77 (4)
C(22)	2208 (5)	364 (4)	876 (4)	86 (5)

$$* \ \bar{U}_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

Table 5. *Bond distances* (Å) *and angles* (°)

	(1)	(2)	(3)
C(1)–C(2)	1·364 (8)	1·380 (17)	1·389 (4)
C(1)–C(6)	1·382 (8)	1·368 (15)	1·401 (5)
C(2)–C(3)	1·395 (7)	1·414 (15)	1·379 (5)
C(3)–C(4)	1·402 (7)	1·414 (15)	1·434 (4)
C(3)–N(1)	1·430 (7)	1·448 (16)	1·479 (4)
C(4)–C(5)	1·401 (7)	1·419 (16)	1·429 (5)
C(4)–N(7)	1·363 (7)	1·324 (13)	1·370 (4)
C(5)–C(6)	1·371 (7)	1·364 (15)	1·378 (5)
N(7)–N(8)	1·334 (5)	1·368 (13)	1·362 (4)
N(8)–C(9)	1·278 (6)	1·282 (12)	1·308 (4)
C(9)–C(20)	1·480 (8)	—	1·504 (5)
C(9)–C(10)	1·491 (9)	1·513 (16)	1·523 (5)
C(9)–C(9ⁱ)	—	1·462 (20)	—
C(20)–O(21)	1·209 (8)	—	1·229 (5)
C(20)–C(22)	1·475 (11)	—	1·535 (6)
C(1)–N(2)	—	—	1·470 (4)
N(1)–O(1)	1·211 (6)	1·245 (11)	1·232 (4)
N(1)–O(2)	1·210 (7)	1·210 (10)	1·216 (4)
N(2)–O(3)	—	—	1·218 (4)
N(2)–O(4)	—	—	1·240 (4)
C(2)–C(1)–C(6)	119·0 (5)	118·1 (11)	120·8 (3)
C(2)–C(1)–N(3)	—	—	120·1 (3)
C(6)–C(1)–N(3)	—	—	119·1 (3)
C(1)–C(2)–C(3)	120·3 (5)	120·6 (10)	120·7 (3)
C(2)–C(3)–C(4)	121·4 (5)	121·3 (12)	120·8 (3)
C(2)–C(3)–N(1)	116·9 (4)	115·4 (11)	117·5 (3)
C(4)–C(3)–N(1)	121·7 (4)	123·2 (11)	121·7 (3)
C(3)–C(4)–C(5)	116·9 (5)	115·5 (11)	116·3 (3)
C(3)–C(4)–N(7)	122·7 (4)	124·4 (11)	121·8 (3)
C(5)–C(4)–N(7)	120·4 (4)	120·1 (10)	121·9 (3)
C(4)–C(5)–C(6)	120·8 (5)	121·6 (11)	122·7 (3)
C(1)–C(6)–C(5)	121·6 (5)	122·9 (13)	118·7 (3)
C(4)–N(7)–N(8)	119·7 (5)	121·5 (11)	119·1 (3)
N(7)–N(8)–C(9)	118·2 (5)	117·4 (10)	115·3 (3)
N(8)–C(9)–C(20)	114·7 (5)	—	114·6 (3)
N(8)–C(9)–C(10)	126·1 (5)	123·9 (9)	126·5 (3)
C(20)–C(9)–C(10)	119·2 (5)	—	118·9 (3)
C(9)–C(9ⁱ)–C(20)	—	120·4 (9)	—
C(9)–C(9ⁱ)–N(8)	—	115·7 (10)	—
C(9)–C(20)–O(21)	117·8 (5)	—	117·7 (4)
C(9)–C(20)–C(22)	119·6 (5)	—	118·7 (3)
O(21)–C(20)–C(22)	122·5 (6)	—	123·6 (3)
C(3)–N(1)–O(1)	121·9 (5)	116·4 (10)	120·3 (3)
C(3)–N(1)–O(2)	118·0 (5)	119·9 (10)	118·0 (3)
O(1)–N(1)–O(2)	120·0 (6)	123·8 (12)	121·7 (3)
C(1)–N(2)–O(3)	—	—	118·5 (3)
C(1)–N(2)–O(4)	—	—	118·5 (3)
O(4)–N(2)–O(3)	—	—	122·9 (3)

Symmetry element: (i) $-x, -y, 1 - z$.

of an o-NO_2 group as the common structural unit. The fact that there is little variation in δ_{NH} throughout the series eliminates any further NH involvement either with solvent molecules or with α-oxo groups [possible for (1) and (3) should they have adopted a Z conformation] and suggests an E conformation for the mono-derivatives and an E,E conformation for the bis-derivative. Analytical and mass-spectral data (Table 1) confirm the absence of any coordinated solvent molecules. Methyl groups associated with the butanedione fragment are clearly non-equivalent and appear as two sharp singlets in the regions δ_{CH_3} 2·08–2·17 and δ_{CH_3} 2·50–2·53. From the IR data there is very little variation in the NH band profile between the series. One intense $\nu(NH)$ band located in the region 3300–3326 cm^{-1} is consistent with a shift to low energy

on hydrogen-bond formation. Aside from very minor features mull and solution spectra are identical.

The three structures are shown in Figs. 1, 2 and 3 which also indicate the common atomic-numbering scheme. All three structures exhibit the E form in preference to the Z form. Thus both structures (1) and (3) show the E form in which the carbonyl oxygen O(21) is not hydrogen bonded to H(7). In the alternative Z form, a bifurcated hydrogen bond would have been formed from H(7) to O(21) as well as to O(1).

This is a rather surprising outcome as our previous studies of phenylhydrazone structures suggest that formation of intra- and intermolecular hydrogen bonds is the most important feature in the structure.

All three structures contain a strong $N(7)-H(7)\cdots O(1)$ intramolecular hydrogen bond. Dimensions for $N\cdots O$, $H\cdots O$ and $N-H\cdots O$ are 2·62 (1), 1·99 (5) Å, 129 (4)° in (1), 2·61 (1), 2·14 (9) Å, 124 (9)° in (2) and 2·64 (1), 1·94 (4) Å, 128 (3)° in (3).

The structure of (1) can be compared with that of the p-nitro compound (5) which also has the E conformation (Willey & Drew, 1983). In that structure the carbonyl group forms an intermolecular hydrogen bond to the N(7) hydrogen forming a polymeric chain along a screw axis.

This association is not observed in (1) presumably because H(7) already forms an intramolecular hydrogen bond to the o-nitro group. This means that the carbonyl O(21) cannot approach H(7) without getting too close to this o-nitro group or indeed to the methyl group C(10).

The closest intermolecular contact involving O(21) is >3·3 Å. This makes it even more surprising that the E conformation is found as with the Z conformation there would be a bifurcated hydrogen bond. It was argued with the p-nitro compound (5) that the E form could be stabilized by the formation of the intermolecular hydrogen bond (although we recognize that the intermolecular hydrogen bond is weaker than that of the more common intra- type) but no such argument is possible for (1).

However, we note a recent study (Taylor, Kennard & Versichel, 1984) of the bifurcated (or three-centre hydrogen bond). They find very few examples (compared to the normal two-centre hydrogen bond) and note that the majority are due to the fortuitous proximity of a proton and an acceptor atom in the same molecule. This might confirm that there is very little increase in stabilization energy of the bifurcated over the normal hydrogen bond and could well account for the frequency of E conformations in the current series of structures. Clearly our determination of a series of structures in different space groups has established that packing effects can be eliminated as a possible cause.

The structure of (3) contains both o- and p-nitro groups. Again there is no intramolecular hydrogen
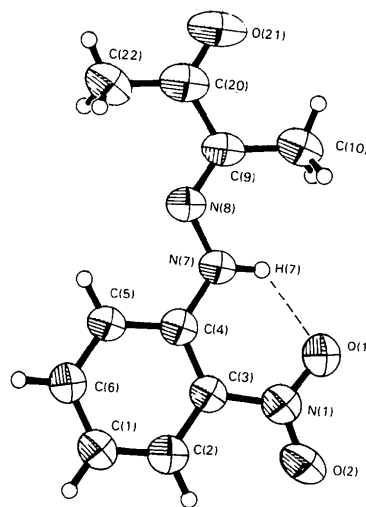

Fig. 1. The structure of (1). 50% probability ellipsoids are shown. For clarity hydrogen atoms are given a fixed radius. The intramolecular hydrogen bond is shown as a dotted line.
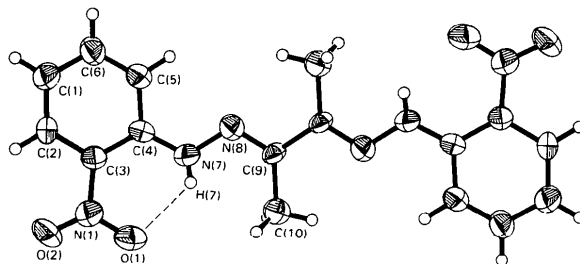

Fig. 2. The structure of (2). 50% probability ellipsoids are shown. For clarity hydrogen atoms are given a fixed radius. The intramolecular hydrogen bond is shown as a dotted line.
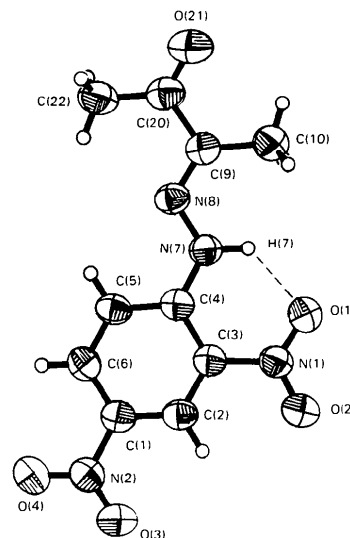

Fig. 3. The structure of (3). 50% probability ellipsoids are shown. For clarity hydrogen atoms are given a fixed radius. The intramolecular hydrogen bond is shown as a dotted line.

bond involving H(7) with the carbonyl oxygen or intermolecular association with a *p*-nitro group. We ascribe this, as before, to the steric constraints of the *o*-nitro group and the methyl group at C(20) which largely surround the hydrogen on N(7).

(2) is centrosymmetric and exhibits the *E,E* conformation. This structure can be compared with that of (6) whose structure was determined with two molecules of DMF (Willey & Drew, 1983). The solvent was hydrogen bonded to the two H(7) atoms in the dimer. In (2) the *o*-nitro group and the methyl group at C(10) effectively shield the H(7) atom from solvent participation in a hydrogen bond. H(7) atoms are hydrogen bonded to the *o*-nitro group at O(1).

The individual dimensions in (1), (2) and (3) follow the pattern established in previous structures in that the dimensions of the phenylhydrazone skeleton are very dependent upon the presence of intramolecular hydrogen bonding between carbonyl oxygen and N(7). Thus with such a bond, the C(4)—N(7), N(7)—N(8), and N(8)—C(9) bond lengths are 1·400, 1·307, 1·313 Å and without such a bond 1·36, 1·39, 1·28 Å. (These are average values from 18 and nine structures respectively, Willey & Drew, 1983, and references therein.) Present dimensions are in (1) 1·363 (7), 1·334 (5), 1·278 (6) Å; in (2) 1·324 (13), 1·368 (13), 1·282 (12) Å and in (3) 1·370 (4), 1·362 (4) and 1·308 (4) Å so they fit in well with the pattern.

Least-squares-planes' calculations show that the molecules are slightly distorted from planarity. The *o*-nitro groups are twisted by angles of 12·1 (1), 5·4 (1), 1·6 (1)° from the plane of the benzene ring. In (3) the *p*-nitro group is twisted by 2·6 (1)°. The angle between the plane of atoms C(9), C(10) and C(20) and the benzene ring is an indication of the steric strain between the methyl group at C(10) and the N(7) hydrogen atom. In the three structures this angle is 6·3 (1),

5·6 (1), 5·0 (1)°, respectively, showing that the repulsions between the C(10) methyl group and H(7) are of minor import, though it is clear from the figures that the arrangement of the hydrogen atoms at C(10) is such as to maximize such contacts.

In the three structures there are no intermolecular contacts less than the sum of van der Waals radii.

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Structure of (*E*)-4,4-Dimethyl-1-(1-naphthyl)-1-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-one, C₁₉H₁₉N₃O

BY S. K. BRANCH*

School of Pharmacy and Pharmacology, University of Bath, Claverton Down, Bath BA2 7AY, England

AND I. W. NOWELL

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, England

Abstract. $M_r = 305\cdot4$, $P2_1/c$, $a = 18\cdot971$ (7), $b = 16\cdot763$ (5), $c = 10\cdot902$ (5) Å, $\beta = 104\cdot64$ (4)°, $V = 3354\cdot4$ Å³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $Z = 8$ (two independent molecules per asymmetric unit), $D_m = 1\cdot20$ (2), $D_x = 1\cdot21$ g cm⁻³, $\mu = 0\cdot83$ cm⁻¹, $F(000) = 1296$, room temperature, final $R = 0\cdot0847$ for 1268

* To whom correspondence should be addressed.