Crystal and Molecular Structures of Butan-2-one *p*-Nitrophenylhydrazone (1), Propanal 2,4-Dinitrophenylhydrazone (2), Dimethyl 2-Oxopropanedioate Phenylhydrazone (3), and Dimethyl 2-Oxopropanedioate 2,4-Dinitrophenylhydrazone (4): Hydrogen Bonding and Bond Order in Phenylhydrazones

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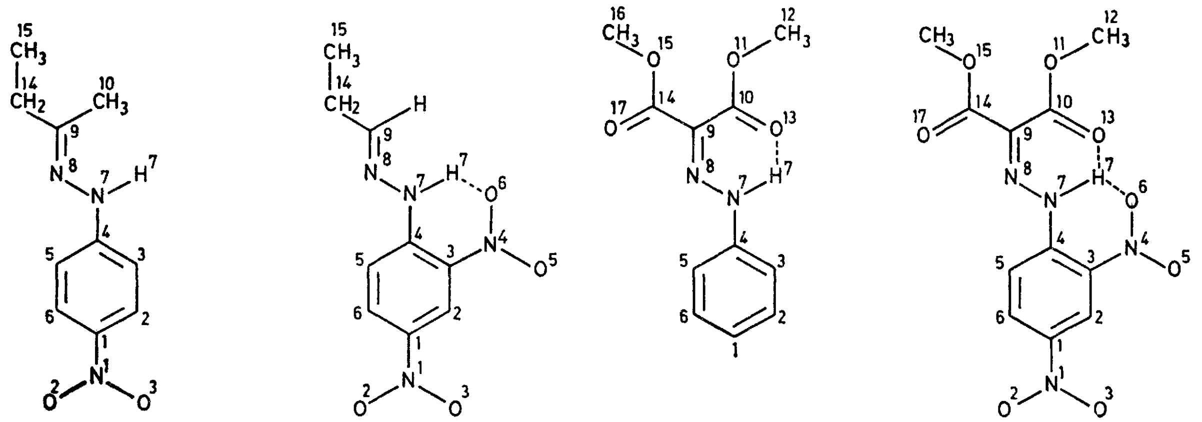
Crystals of the title compound (1), $C_{10}H_{13}N_3O_2$, are monoclinic, a = 4.119(11), b = 18.992(12), c = 13.992(10) Å, β = 96.0(1)°, space group $P2_1/c$, Z = 4. Compound (2), $C_9H_{10}N_4O_4$, is monoclinic a = 5.333(7), b = 11.488(8), c = 17.713(10) Å, β = 95.0(1)°, space group $P2_1/c$, Z = 4. Compound (3), $C_{11}H_{12}N_2O_4$, is monoclinic, a = 21.331(14), b = 4.153(10), c = 13.640(12) Å, β = 102.8(1)°, space group $P2_1/a$, Z = 4. Compound (4), $C_{11}H_{10}N_4O_8$, is monoclinic, a = 11.198(8), b = 14.779(9), c = 8.443(7) Å, β = 92.4(1)°, space group $P2_1/a$, Z = 4. All four 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) 330, 0.103; (2) 611, 0.059; (3) 863, 0.061; and (4) 1 274, 0.070, respectively. In all cases the (NO_2)–Ar–NH–N=C–(C=O) fragment is essentially planar. The $NO_2 \cdots$ HN and C=O $\cdots$ HN separations suggest that there is substantial intramolecular hydrogen bonding. In addition in compound (2) there is evidence for intermolecular as well as intramolecular $NO_2 \cdots$ H–N bonding in the crystal. In phenylhydrazones whose structures are known, there is an inverse relationship between Ar–NH and N–N bond lengths, and a direct relationship between Ar–N(H) and N=C bond lengths.

IN previous work [1] we studied the spectroscopic properties of a wide range of phenylhydrazones particularly with respect to hydrogen bonding. We found that *o*-nitro or *o*-carbonyl groups formed strong hydrogen bonds to the N–H group which were readily observed by ^{1}H n.m.r. but not by i.r. spectroscopy. Terminal carbonyl groups as in (3) also formed strong hydrogen bonds to the N–H group and these could be detected by both ^{1}H n.m.r. and i.r. spectroscopy. When both *o*-nitro or *o*-carbonyl groups and terminal carbonyl groups were present the N–H hydrogen atom was doubly hydrogen bonded, and this was apparent in the ^{1}H n.m.r. spectrum. In order to confirm the presence of the proposed hydrogen bonding we have determined the structures of four of the previously studied compounds [(1)—(4)] by *X*-ray crystallography. These compounds were chosen since potentially they could show no intramolecular hydrogen bonding (1), $NO_2 \cdots$ H–N bonding (2), C=O $\cdots$ HN bonding (3), and both types of hydrogen bonding (4).



(1) (2) (3) (4)

Compounds (1)—(4) with crystallographic numbering scheme

EXPERIMENTAL

In the four cases, needle shaped crystals suitable for *X*-ray crystallography were obtained by slow evaporation of methanolic solutions. Preparative details for these compounds have been given.[1] Crystal data are given in Table 1.

Crystallographic Measurements and Structure Analysis.—Each of the four crystals was mounted on a General Electric XRD5 diffractometer which was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation (λ = 0.710 7 Å) was used. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background against 2θ. Absorption and extinction corrections were not applied.

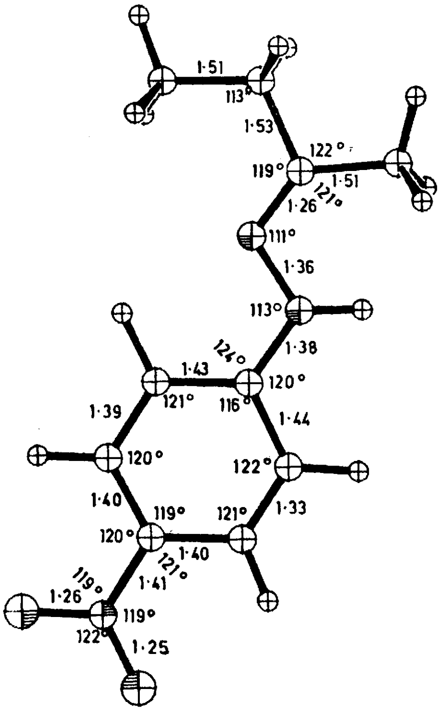


FIGURE 1 Molecular dimensions for compound (1). Bond lengths in Å. Mean standard deviations are 0.005 Å, 3°

All four structures were solved by the statistical method using the SHEL-X-76 system of programs.[2] All structures were refined using full-matrix least squares with a weighting scheme that gave similar values of $\omega\Delta^2$ with ranges of F_o and $(\sin\theta)/\lambda$ *viz.*, $\omega^{\frac{1}{2}} = 1$ for $F_o < F^*$ and $\omega^{\frac{1}{2}} = F^*/F_o$ for $F_o > F^*$ (values of F^* are given in Table 2). For all structures hydrogen atoms were fixed in trigonal or tetrahedral positions at 1.08 Å from the carbon atoms and their thermal parameters were allowed to refine. When the thermal parameter refined to an unreasonable value it was fixed at the same value as the carbon atom to which it was bonded. H(7) on N(7) was allowed to refine freely in (4) but with the N–H bond length constrained to 1.00(5) Å in (1)—(3). Scattering factors were taken from ref. 3. Calculations were made on the CDC 7600 computer at the University of London Computer Centre. The final difference-Fourier maps were featureless. Zero-weighted reflections gave no large discrepancies. Data collection and refinement details are given in Table 2. Details of interatomic distances and co-ordinates are listed in Tables 3—6. Bond lengths and bond angles are shown in Figures 1—4. Table 7 lists least-squares-plane calculations. The anisotropic thermal parameters, observed and calculated structure factors, and hydrogen atom parameters are listed in Supplementary Publication No. SUP 22925 (26 pp.).*

TABLE 1

Crystal data

Compound	(1)	(2)	(3)	(4)
Formula	$C_{10}H_{13}N_3O_2$	$C_9H_{10}N_4O_4$	$C_{11}H_{12}N_2O_4$	$C_{11}H_{10}N_4O_8$
M	207.1	238.1	236.1	326.1
Crystal class	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/a$	$P2_1/a$
a(Å)	4.119(11)	5.333(7)	21.331(14)	11.198(8)
b(Å)	18.992(12)	11.488(8)	4.153(10)	14.779(9)
c(Å)	13.992(10)	17.713(10)	13.640(12)	8.443(7)
β(°)	96.0(1)	95.0(1)	102.8(1)	92.4(1)
U(Å^3)	1 088.6	1 081.2	1 178.1	1 396.0
μ(cm^{-1})	0.98	1.27	1.11	1.45
F(000)	440	496	496	672
D_m (g cm^{-3})	1.25	1.43	1.31	1.52
D_c (g cm^{-3})	1.26	1.46	1.33	1.15
Z	4	4	4	4

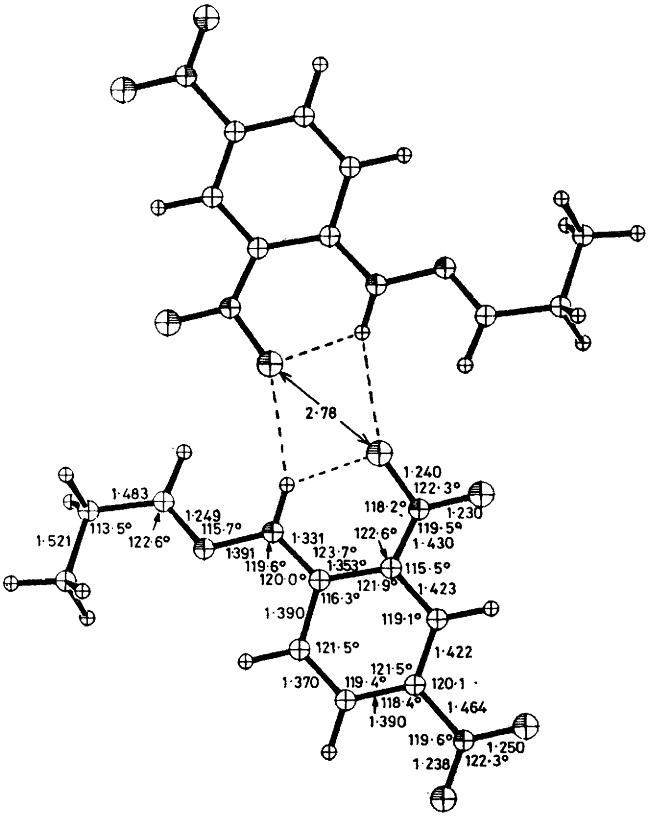


FIGURE 2 Molecular dimensions for compound (2). Bond lengths in Å. Mean standard deviations are 0.018 Å, 1.3°

DISCUSSION

In a previous paper,[1] we showed that the chemical shifts for the NH protons in the compounds under discussion were: (1) δ 7.7; (2) 11.0; (3) 12.9; and (4) 14.3 (all in $CDCl_3$).† We had proposed that the series reflected an increase in hydrogen bond strength. Thus (1) forms no intramolecular hydrogen bonds; (2) and (3) form $NO_2\cdots HN$ and $C{=}O\cdots HN$ bonds respectively, whilst (4) forms both types of hydrogen bond.

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* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index Issue.

† These compounds were called (Ik), (IIj), (IIIb), and (IVb), respectively, in ref. 1.

TABLE 2

Data collection and refinement details

Compound	(1)	(2)	(3)	(4)
Crystal size (mm)	0.4 × 0.1 × 1.25	0.15 × 0.35 × 1.5	0.75 × 0.4 × 1.2	0.35 × 0.6 × 1.0
Rotation axis	*a* *	*a* *	(110)	*a* *
$2\theta_{max.}$ (Mo-K_α) radiation	35	40	40	40
No. of data measured	696	1 000	1 081	1 734
Criterion for data inclusion	$I > \sigma$ (I)	$I > \sigma$ (I)	$I > \sigma$ (I)	$I > 2\sigma$ (I)
No. of data used in refinement	330	611	863	1 274
F * in weighting scheme	40	65	70	25
Final *R* value	0.103	0.059	0.061	0.070

It is apparent that compounds (1)—(4) have structures which are consistent with the ^{1}H n.m.r. data. However, there are some remarkable variations in bond lengths which are discussed below. We shall first discuss each structure in turn.

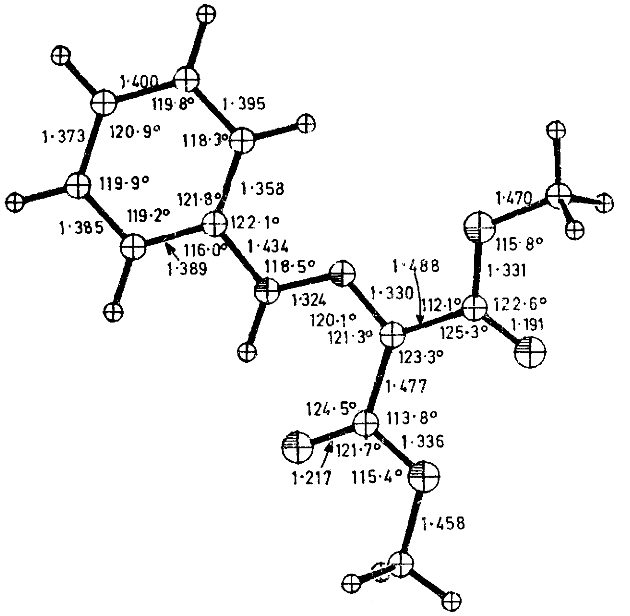

FIGURE 3 Molecular dimensions for compound (3). Bond lengths in Å. Mean standard deviations are 0.016 Å, 1.1°

In compound (1) (Figure 1) nearly all the atoms are coplanar (Table 7). There are no intramolecular hydrogen bonds and only one intermolecular contact less than 3.25 Å (Table 8). The N(7) · · · O(3) distance is 3.00 Å and it appears that a weak hydrogen bond may be formed as the N–H · · · O and H · · · O–N angles are 120 and 121°, respectively.

TABLE 3

Atomic co-ordinates for compound (1) (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
N(1)	1 236(75)	3 108(18)	275(28)
O(2)	145(79)	3 662(14)	617(23)
O(3)	613(65)	2 992(16)	−603(23)
C(1)	3 056(80)	2 608(20)	855(27)
C(6)	4 161(82)	1 995(19)	442(30)
C(5)	5 968(78)	1 504(17)	1 014(26)
C(4)	6 767(78)	1 623(23)	2 018(27)
C(3)	5 483(84)	2 255(20)	2 396(27)
C(2)	3 800(76)	2 723(20)	1 841(24)
N(7)	8 652(68)	1 170(18)	2 613(22)
N(8)	9 505(73)	575(18)	2 153(26)
C(9)	11 375(78)	196(22)	2 708(31)
C(10)	12 535(84)	269(19)	3 766(28)
C(11)	12 523(90)	−513(20)	2 351(28)
C(12)	11 423(88)	−648(21)	1 301(27)

In compound (2) (Figure 2) an intramolecular hydrogen bond is formed between H(7) and O(6) of length 1.92 Å [the N(7) · · · O(6) distance is 2.61 Å]. This oxygen atom is also involved in a short intermolecular contact, O(6) · · · O(6^{I}) 2.78 Å, across a centre of symmetry. This mode of packing of pairs of molecules appears to be determined by intermolecular hydrogen bonding, H(7) · · · O(6^{I}) and H(7^{1}) · · · O(6) *ca.* 2.1 Å. Both nitro-groups are almost coplanar with the benzene ring (Table 7).

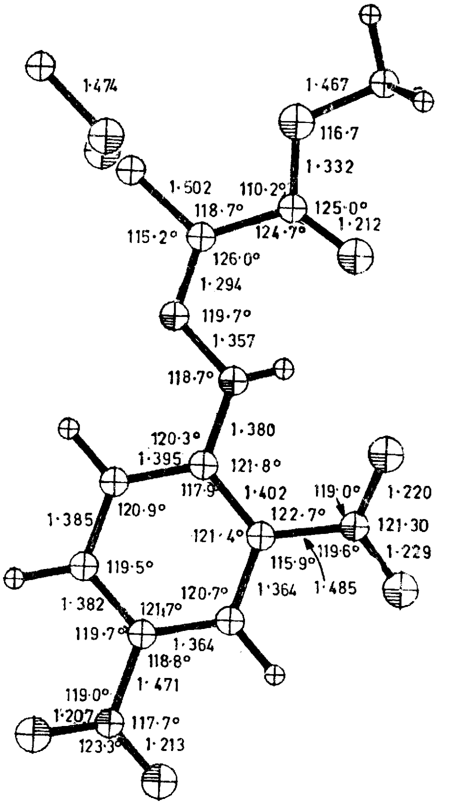

FIGURE 4 Molecular dimensions for compound (4). Bond lengths in Å. Mean standard deviations are 0.012 Å, 0.8°

In compound (3) an intramolecular hydrogen bond is formed between O(13) of the CO_2Me group and H(7) (Figure 3). Atomic separations are N(7) · · · O(13) 2.57, H(7) · · · O(13) 1.79 Å. As would be expected the formation of this hydrogen bond leads to the CO_2Me

group being almost coplanar with the benzene ring (Table 7), the angle of intersection being 9.2°. Thus atoms H(7), N(7), N(8), C(9), C(10), and O(13) form an approximate hexagon. The other CO_2Me group intersects the benzene ring plane at an angle of 16.3°. There are no close intermolecular contacts in this case.

TABLE 4

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

Atom	x	y	z
C(1)	2 579(26)	1 751(12)	1 880(8)
C(2)	4 452(23)	2 082(12)	1 443(7)
C(3)	5 743(24)	1 256(12)	1 089(7)
C(4)	5 242(24)	49(12)	1 171(7)
C(5)	3 286(24)	−243(12)	1 635(7)
C(6)	2 003(25)	585(11)	1 984(8)
N(1)	1 157(24)	2 632(11)	2 261(7)
O(2)	1 788(19)	3 674(9)	2 203(6)
O(3)	−604(19)	2 332(10)	2 618(6)
N(4)	7 633(20)	1 682(11)	635(6)
O(5)	8 053(17)	2 734(9)	613(6)
O(6)	8 816(18)	966(9)	281(6)
N(7)	6 543(21)	−788(9)	864(6)
N(8)	5 896(21)	−1 946(9)	968(6)
C(9)	7 397(27)	−2 683(12)	750(8)
C(14)	6 989(30)	−3 954(12)	820(10)
C(15)	4 452(32)	−4 267(13)	1 096(10)

For compound (4) H(7) is hydrogen bonded to both O(13) of the CO_2Me group (Figure 4) and O(6) of the *o*-nitro-group. N(7) is 2.70 Å from O(13), and 2.62 Å from O(6). H(7) is equidistant from both oxygens at 2.07 and 2.08 Å, respectively. It will be noted that these H · · · O separations are slightly longer than those in (2) and (3). The results from our ^1H n.m.r. studies are consistent with these data. The NH chemical shift increases between compounds (2) and (3) (see above) while the H(7) · · · O distance becomes shorter and the bond presumably becomes stronger. The formation of two hydrogen bonds simultaneously increases both NH · · · O separations, presumably because the most favourable configuration for hydrogen bonding cannot be taken up to both oxygen atoms at the same time. Also the effect of double hydrogen bonding does not have an additive effect on the proton chemical shift (see values above) in agreement with the crystallographic data.

TABLE 5

Atomic co-ordinates for compound (3) ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
C(1)	2 745(6)	13 588(27)	6 412(9)
C(2)	2 101(5)	13 015(28)	5 952(9)
C(3)	1 714(5)	11 266(25)	6 461(8)
C(4)	1 985(5)	10 161(27)	7 421(8)
C(5)	2 617(5)	10 852(26)	7 893(8)
C(6)	2 998(5)	12 546(28)	7 374(9)
N(7)	1 628(4)	8 279(22)	7 992(7)
N(8)	1 064(4)	7 096(22)	7 527(6)
C(9)	731(5)	5 247(27)	8 025(8)
C(19)	114(5)	3 974(29)	7 419(9)
O(11)	46(3)	4 565(22)	6 442(5)
C(12)	−553(6)	3 406(36)	5 786(9)
O(13)	−283(4)	2 600(24)	7 749(6)
C(14)	981(6)	4 434(27)	9 094(8)
O(15)	578(3)	2 653(21)	9 491(5)
C(16)	803(6)	1 850(32)	10 551(8)
O(17)	1 504(4)	5 261(23)	9 585(5)

TABLE 6

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

Atom	x	y	z
C(3)	1 394(7)	1 800(5)	3 873(9)
C(4)	2 091(7)	2 465(5)	4 653(8)
C(5)	1 761(7)	3 367(6)	4 429(10)
C(6)	787(8)	3 596(6)	3 446(10)
N(1)	−934(7)	3 160(7)	1 691(9)
O(2)	−1 637(7)	2 575(6)	1 297(9)
O(3)	−1 036(8)	3 942(6)	1 271(11)
N(4)	1 675(8)	844(5)	3 976(9)
O(5)	946(8)	296(5)	3 453(13)
O(6)	2 629(6)	601(4)	4 614(8)
N(7)	3 070(6)	2 245(5)	5 631(9)
N(8)	3 670(6)	2 920(4)	6 409(8)
C(9)	4 575(7)	2 728(5)	7 353(9)
C(10)	5 055(7)	1 815(6)	7 687(10)
O(11)	6 021(5)	1 866(4)	8 658(8)
C(12)	6 614(9)	1 010(7)	9 084(14)
O(13)	4 626(5)	1 120(4)	7 157(8)
C(14)	5 130(8)	3 521(6)	8 219(11)
O(15)	6 056(5)	3 849(4)	7 517(7)
C(16)	6 695(9)	4 596(7)	8 339(13)
O(17)	4 757(7)	3 808(5)	9 421(9)

TABLE 7

Least-squares-plane calculations (Å) through atoms C(n) (n = 1—6 inclusive). Deviations of other atoms from that plane are also listed

Compound	(1)	(2)	(3)	(4)
C(1)	0.00	−0.01	0.01	0.00
C(2)	0.01	0.01	−0.00	0.01
C(3)	−0.02	−0.00	−0.02	−0.01
C(4)	0.02	0.00	0.02	0.00
C(5)	−0.01	−0.00	−0.00	0.00
C(6)	0.00	0.00	−0.01	−0.01
N(1)	0.01	−0.01		0.00
O(2)	−0.00	0.07		0.26
O(3)	0.01	−0.08		−0.27
N(4)		−0.01		−0.06
O(5)		0.04		0.12
O(6)		−0.06		−0.26
N(7)	0.06	0.06	0.05	0.01
N(8)	0.00	0.04	0.32	0.08
C(9)	0.14	0.27	0.41	0.12
C(10)	0.21		0.24	0.09
C(14)	0.03	0.03	0.74	0.28
A(°)	1.0	2.8		14.4
B(°)		4.1		10.4
C(°)			9.2	1.9
D(°)			16.3	85.0

A—D are the angles of intersection between the benzene ring plane and other planes, *viz.* A, N(1), O(2), O(3); B, N(4), O(5), O(6); C, C(10), O(11), C(12), O(13); D, C(14), O(15), C(16), O(17).

TABLE 8

Intermolecular distances <3.25 Å in the four structures

Compound	Atoms	Distance (Å)	Symmetry element *
(1)	N(7) · · · O(3)	3.00	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$
(2)	C(2) · · · O(3)	3.23	$1 + x, y$
	O(6) · · · O(6)	2.78	$2 - x, -y, -z$
	O(5) · · · N(1)	3.23	$1 + x, y, z$
	O(3) · · · C(9)	3.23	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(3)	None		
(4)	O(17) · · · C(2)	3.25	$x, \frac{1}{2} - y, 1 + z$
	O(17) · · · O(2)	3.07	$x, \frac{1}{2} - y, \frac{1}{2} + z$
	O(15) · · · N(4)	3.13	$\frac{1}{2} + x, \frac{1}{2} - y, z$
	O(15) · · · O(6)	3.18	$\frac{1}{2} + x, \frac{1}{2} - y, z$
	O(15) · · · N(7)	3.25	$\frac{1}{2} + x, \frac{1}{2} - y, z$
	C(4) · · · N(2)	3.22	$\frac{1}{2} + x, \frac{1}{2} - y, z$
	O(3) · · · C(12)	3.14	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
	C(14) · · · O(5)	3.19	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
	O(15) · · · O(5)	3.18	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$

* The first atom is at x, y, z. The second atom has this symmetry element applied to it.

In (4) both nitro-groups are twisted out of the plane of the benzene ring, about the ring–N axis, by angles of 14.4 (*ortho*) and 10.4° (*para*). The reason for this is unclear since the nitro-groups in compounds (1) and (2) are planar. It has however been shown that while nitrobenzene is planar,[4] in *m*-dinitrobenzene the nitro-groups are inclined to the ring plane at an angle of 11°.[5] One cannot visualise any steric reason for this inclination in this last compound.

The CO_2Me group which is hydrogen bonded to NH is virtually planar with the ring (Table 7); the second CO_2Me group, which is not involved in hydrogen bonding, is twisted out of the ring plane by an angle of 85°. There are a number of short intermolecular contacts for (4) (Table 8) but none of these are indicative of hydrogen bonding. In this case the close packing of two molecules, as seen in (2), is prevented by the presence of the hydrogen-bonded CO_2Me group.

TABLE 9

Bond lengths (Å) for the $>C(4)–N(7)H(7)–N(8)=C(9)$ fragment in a series of phenylhydrazones

Compound	Reference	C(4)–N(7)	N(7)–N(8)	N(8)–C(9)
(A) Compounds having no terminal group conjugating with the N(8)=C(9) bond				
(1) [a]	This work	1.38	1.36	1.26
(2) [b]	This work	1.331	1.391	1.249
(5) [c]	6	1.350	1.424	1.304
(6) [d]	7	1.356	1.399	1.269
(7) [e]	8	1.361	1.400	1.300
(8) [f]	9	1.353	1.372	1.284
(9) [g]	10	1.351	1.417	1.273
(10) [h]	11	1.403	1.354	1.284
(11) [i]	12	1.372	1.369	1.254
Mean		1.361	1.39	1.28
Standard deviations		0.021	0.025	0.019
Mean bond order		1.5	1.2	1.9
(B) Compounds having terminal groups conjugating to the N(8)=C(9) bond				
(12) [j]	13	1.423	1.360	1.314
(3) [k]	This work	1.434	1.324	1.330
(4) [l]	This work	1.380	1.357	1.294
(13) [m]	14	1.394	1.333	1.312
(14) [n]	15	1.416	1.308	1.313
(15) [o]	16	1.36	1.33	1.27
(16) [p]	17	1.410	1.345	1.331
(17) [q]	18	1.425	1.361	1.308
Mean		1.41	1.34	1.31
Standard deviation		0.025	0.019	0.020

[a] Butan-2-one *p*-nitrophenylhydrazone (1). [b] Propanal 2,4-dinitrophenylhydrazone (2). [c] Propanone *p*-nitrophenylhydrazone (5). [d] 5-Bromomethylenecyclononanone 2,4-dinitrophenylhydrazone (6). [e] *p*-Dimethylaminobenzaldehyde *p*-nitrophenylhydrazone hydrochloride (7). [f] *p*-Methylbenzophenone 2,4-dinitrophenylhydrazone (8). [g] Propanone *m*-nitrophenylhydrazone (9). [h] Benzoyl chloride phenylhydrazone (10). [i] Mannose *p*-bromophenylhydrazone (11). [j] 2-Oxopropanal phenylhydrazone (12). [k] Dimethyl 2-oxopropanedioate phenylhydrazone (3). [l] Dimethyl 2-oxopropanedioate 2,4-dinitrophenylhydrazone (4). [m] 1,2-naphthoquinone 1-(4-chloro-2-nitrophenylhydrazone) (13). [n] Dehydroascorbic acid *p*-bromophenylhydrazone (14). [o] α-(4-Chloro-2-nitrophenylazoacetoacetanilide) (15). [p] 1-(*p*-Nitrophenylazo)naphthalene-2-carbaldehyde (quinonoid form) (16). [q] Bis[2,6-diacetylpyridiniumbis(phenylhydrazone)] uranyl tetrachloride (17).

We have searched the Cambridge Data Centre files for fragments of the type $R^1R^2C_6H_3NH–N=C<$ and the dimensions of the compounds extracted from the files are given in Table 9. In all the phenylhydrazones listed in Table 9 the ring–N(7)H(7)N(8)O(9) moiety has been found to be planar. This suggests that the N(7) atoms are sp^2 hybridised with the lone pair of electrons in a p_z orbital.* This lone pair is then able to conjugate with the aromatic ring and with the N(8)=C(9) bond. Dewar[19] has stated that the ring–N(7) π-interaction in comparable systems must be large in order to make the N(sp^2) configuration the preferred form rather than N(sp^3). It seems clear that in these phenylhydrazones there is considerable conjugation from the N(8)=C(9) bond *via* N(7) to the aromatic ring. Evidence to support this is provided by the C–C and C–N bond lengths. It has been shown that for C–C bonds with bond orders between one and two that there is a straight line relationship between bond length and bond order.[20] If we assume that a similar relationship holds for C–N and N–N bonds we can obtain equations relating bond length to bond order and use these to determine bond orders in phenylhydrazones. For C–N bonds, for a bond order of unity we shall use the C–N bond length of methylamine which is 1.47 Å.[21] In molecular orbital calculations 1.27 Å has been taken as the C=N bond length;[22] in two of the compounds quoted in Table 9 however this bond length is 1.25 Å so we shall use this as the bond length for bond order two. Use of these values gives equation (1).

$$\text{Bond order C–N} = -4.54\,(\text{Bond length C–N}) + 7.68 \qquad (1)$$

For N–N single bonds we shall use the N–N single bond length for hydrazine, 1.45 Å,[23] and for N=N bonds the value of 1.24 Å given by Dewar.[22] These lead to equation (2).

$$\text{Bond order N–N} = -5.56\,(\text{Bond length N–N}) + 8.89 \qquad (2)$$

In Table 9 we show bond lengths for 17 phenylhydrazones whose molecular dimensions are known accurately. We have divided these compounds into two groups: those without terminal carbonyl or other conjugating groups (set A) and those with such groups (set B). Taking the compounds as a whole we have discovered interesting relationships between certain bond lengths; thus the C(4)–N(7) bond length is inversely proportional to the N(7)–N(8) bond length (correlation −0.69) and directly proportional to the N(8)–C(9) bond length (correlation 0.73).

To explain this we assume that changes in the groups which are attached to the ring–N(7)–N(8)–C(9) fragment will have an effect on the electron density within this moiety. If we first consider a molecule which has no terminal carbonyl groups, conjugation of N(7) with the ring would lead to a transfer of electron density to the

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* In our work the positions of the hydrogen atoms were not determined accurately enough for us to be completely certain that the N(7) atoms are not slightly pyramidal. But non-planarity seems unlikely from the C(4)–N(7)–C(8) angle (Table 10) and the least-squares-plane (Table 7).

ring and give predicted bond orders, *viz.* C(4)–N(7) > 1, N(8)–C(9) *ca.* 2, and N(7)–N(8) *ca.* 1. This is borne out in our calculated bond order data for these compounds [Table 9(A)].

On considering molecules which possess terminal carbonyl group(s), set B, canonical form descriptions indicate a relative increase in the bond order of the N(7)–N(8) linkage with a corresponding decrease in bond order of the C(4)–N(7) and N(8)–C(9) bonds, respectively. Results are given in Table 9(B). A comparison of bond lengths for the two sets of compounds gives: C(4)–N(7) set B (mean 1.41 Å) > set A (mean 1.361 Å); N(8)–C(9) set B (mean 1.31 Å) > set A (mean 1.28 Å); N(7)–N(8) set B (mean 1.34 Å) < set A (mean 1.39 Å). The differences in bond lengths between the two groups of compounds were statistically significant ($p > 0.95$) in every case.

The presence or absence of a carbonyl group seems to be the most significant structural feature for these compounds. However there are concerted changes in bond length from structure to structure within the two groups. Results of a factor analysis [24] on these three bond lengths for the 17 structures show just one factor with components 0.95, — 0.81, 0.82 for the three bonds C(4)–N(7), N(7)–N(8), N(8)–C(9) respectively. This confims that any structure difference in these molecules which affects the electron density of any part of the ring –N(7)–N(8)–C(9) fragment does so in such a way that the conjugated C(4)–N(7) and N(8)–C(9) bond orders increase while the N(7)–N(8) bond order decreases and *vice versa*.

TABLE 10

Bond angles for the $\genfrac{}{}{0pt}{}{-C^3}{-C^5}\!\!>\!-C^4-N^7H^7-N^8{=}C^9-$fragment in a series of phenylhydrazones

(A) Compounds having no nitro-group (compounds are numbered as in Table 9)

Compound	347	345	547	478	789
(1)	120	116	124	113	111
(5)	116.2	119.6	124.6	115.6	112.3
(7)	117	120	123	117	113
(9)	118.2	120.1	121.6	119.9	117.6
(10)	117.5	120.4	122.1	118.6	120.4
(11)	119.7	117.3	123.0	121.4	117.7
(12)	116.7	119.3	124.0	120.1	115.6
(13)	116.0	121.8	122.1	118.5	120.1
(14)	117.6	119.4	122.9	120.2	117.4
(16)	117.0	120.5	122.5	116.6	117.1
(17)	116.2	123.2	120.6	118.9	116.5
Mean	117.4	119.8	122.8	118.1	116.2
Standard deviation	1.42	1.94	1.16	2.45	3.07

(B) Compounds having an *o*-nitro group

Compound	347	345	547	478	789
(2)	123.7	116.3	120.0	119.6	115.7
(6)	123.9	116.3	119.8	118.7	115.5
(8)	123.6	116.1	120.3	117.5	118.6
(4)	121.8	117.9	120.3	118.7	119.7
(13)	122.4	117.5	120.0	118.1	120.4
Mean	123.1	116.8	120.1	118.5	118.0
Standard deviation	0.93	0.82	0.22	0.78	2.3

Variations are also observed in the bond angles; in particular the presence or absence of an *o*-nitro-group on C(3) affects the geometry at C(4) (Table 10). In the non-nitro-compounds the C(3)–C(4)–N(7) angle is smaller, and the C(3)–C(4)–C(5) and C(5)–C(4)–N(7) angles are larger than those in the *o*-nitro-compounds ($p > 0.95$) (mean values 117.4, 119.8, 122.8°, and 123.1, 116.8, 120.1°, respectively). Scattergrams [25] show that the five bond angles are relatively unaffected by changes in the three bond lengths. The maximum correlation between any of the three bonds and one of the five angles is only 0.36.

With these non-nitro-compounds most C(3)–C(4)–N(7) angles are significantly less than 120° and most C(5)–C(4)–N(7) angles significantly greater than 120°. This clearly suggests that repulsions between N(8) and H(5) are greater than those between H(7) and H(3). With the introduction of the *o*-nitro-group there must be an additional stronger repulsion between H(7) and the nitro-group which is partly relieved by an increase in the C(3)–C(4)–N(7) angle and a decrease in the C(3)–C(4)–C(5) angle. An additional consideration must be the geometry of the N–O • • • H hydrogen bond.

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