# Hydrogen Bonding in Phenylhydrazone Derivatives of Benzophenone: Crystal and Molecular Structures of Benzophenone (2-Nitrophenyl)hydrazone, containing an Intramolecular $NO_2 \cdots NH \cdots \pi$ Bifurcated Hydrogen Bond, and Benzophenone (4-Nitrophenyl)hydrazone, containing an Intramolecular $NH \cdots \pi$ Hydrogen Bond. Comments on Hydrogen Bond Vagaries in Various Types of Phenylhydrazone†

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Crystal structures have been determined of the two title compounds. The (2-nitrophenyl)hydrazone (**2**) is monoclinic, space group $P2_1/a$, $Z = 4$, with $a = 12.074(5)$, $b = 12.771(8)$, $c = 11.998(8)$ Å, $\beta = 118.0°$. The (4-nitrophenyl)hydrazone (**3**) is orthorhombic, space group *Pcab*, $Z = 8$, with $a = 8.468(7)$, $b = 13.98(1)$, $c = 26.82(1)$ Å. Respectively, 1 244 and 1 181 independent reflections above background were collected and the structures were refined to $R$ 0.074 and 0.068. The two structures show remarkably different conformations. In (**2**), the hydrazone N(7)–H(7) group is involved in an intramolecular hydrogen bond to the *ortho*-nitro group, and there is also a possible $H(7) \cdots \pi$ interaction. In (**3**) there is a definite $H(7) \cdots \pi$ interaction with the C–C bond of a phenyl group, with $H(7) \cdots C$ distances of 2.43 and 2.26 Å. The difference between the two structures is probably due to the fact that in (**2**) the hydrogen bond requirements of the N(7)–H(7) group are satisfied by the *ortho*-nitro group, and that in consequence there is no need for much subsidiary overlap with the $\pi$-electrons. In (**3**) there is no *ortho*-group and therefore the hydrogen bond can only be formed with the C–C bond.

Evidence for these $N-H \cdots C-C$ interactions is also obtained from the i.r. spectra of a series of compounds. Frequency difference values [$\nu_{NH}$(crystals) − $\nu_{NH}(CHCl_3)$] of 14—15 cm$^{-1}$ are observed for (**3**) and similar compounds, providing a clear indication of an intramolecular $NH \cdots \pi$ bond in the crystals which does not survive in solution.

Hydrogen bonding between hydroxy groups and $\pi$-electrons of aromatic systems has attracted recent attention primarily from considerations of the contact distance, stereochemistry, and orbital overlaps of the resultant $OH \cdots \pi$ bond.[1–4] In the case of diphenylphenols, location of the hydroxy hydrogen atom in an unsymmetric position away from the six-fold axis and directly linked to two nearest carbon atoms of a benzene ring appears to be a common feature.[5–7] In one case (4-nitro-2,6-diphenylphenol[7]), both intra- and inter-molecular $OH \cdots \pi$ interactions are present in which the OH proton is situated centrally above a C=C bond of each of two proximal phenyl rings (*cf.* benzene–$Ag^+$ complexes[8]).

We seek to establish the existence of similar $NH \cdots \pi$ bonds. A previous study of phenylhydrazone derivatives of benzaldehyde has confirmed that the *E*-configuration is adopted in all cases.[9] This places the phenyl group on the opposite side of the C=N double bond to the substituted anilino group and out of reach of any possible hydrogen bond interaction with N(7)–H(7). However with two such groups present, as in benzophenone phenylhydrazones, an $NH \cdots \pi$ interaction similar to that for $OH \cdots \pi$ bonds in diphenylphenols becomes a real possibility following rotation and suprapositioning of the benzophenone *cis*-phenyl group. This could be enhanced/diminished by the presence of a suitable hydrogen-bond acceptor group in the *ortho*-position of the phenylhydrazone group (*e.g.* $NO_2$), providing an additional binding contact $NH \cdots O_2N$. These considerations are explored in the present structural–spectroscopic study of the benzophenone derivatives (**1**)—(**4**).

## Results and Discussion

Compound (**1**)—(**4**) were obtained by treatment of benzophenone with the appropriate phenylhydrazine in glacial acetic acid–ethanol.[10] Microanalytical and spectral data are collected in Table 1.

*I.r. Data.*—Each phenylhydrazone shows a single NH stretching absorption both in the solid state (Nujol mull) and in solution. For (**1**) and (**3**), frequency-difference values [$\nu_{NH}$(crystals) − $\nu_{NH}(CHCl_3)$] of 14 and 15 cm$^{-1}$ respectively provide a clear indication of an intramolecular $NH \cdots \pi$ bond in the crystals which does not survive in solution. Corresponding difference values for $\nu$(OH) of phenolic systems where an $OH \cdots \pi$ hydrogen bond has been established structurally are: for 2,6-diphenylphenol $\nu_{NH}$(crystals) − $\nu_{NH}(CCl_4)$ = 31.7 cm$^{-1}$;[11] for 4-nitro-2,6-diphenylphenol $\nu_{NH}$(crystals) − $\nu_{NH}(CCl_4)$ = 38.0 cm$^{-1}$.[2] For 2,2-bis-(2-hydroxy-5-methyl-3-t-butylphenyl)propane $\nu_{NH}$(crystals) − $\nu_{NH}(CCl_4)$ is zero,[12] *i.e.* the particular $OH \cdots \pi$ bonded conformation is retained in solution. In the case of (**1**) the observed singlet in $Me_2SO$ solution ($\nu_{NH}$ 3 272 cm$^{-1}$; this represents a low-energy shift of 48 cm$^{-1}$ with respect to $\nu_{NH}$ in the solid state) suggests that for solvent molecules (S) capable of intermolecular hydrogen-bond formation, there is appreciable $NH \cdots S$ bonding.

Clearly the absence of an *ortho*-$NO_2$ group allows the close proximity of solvent molecules, and rather suggests that the

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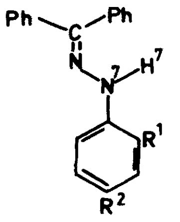
† *Supplementary data available* (SUP 56423, 11 pp.): H-co-ordinates and dimensions involving H, thermal parameters. For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1986. Structure factor tables are available from the editorial office on request.

**Table 1.** Microanalytical and spectral data for phenylhydrazones

| Compound | Formula | Colour | Mol. wt. | M.p. (°C) | Calc./Found (%) C | H | N | $M^+/z$ | $\nu_{NH}$/cm$^{-1}$ | $\delta_{NH}$ | $\lambda_{max.}$/nm$^f$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) | $C_{19}H_{16}N_2$ | Lime | 272.35 | 138—139 | 83.8/83.6 | 5.9/5.8 | 10.3/10.1 | 272 | 3 320$^a$<br>3 334$^b$<br>3 272$^c$ | <br>8.76$^e$ | 25 300sh<br>29 940<br>40 980 |
| (2) | $C_{19}H_{15}N_3O_2$ | Red | 317.35 | 165—166 | 71.9/71.8 | 4.8/4.8 | 13.2/13.1 | 317 | 3 292$^a$<br>3 299$^b$<br>3 289$^c$ | 10.93$^d$<br>10.77$^e$ | 22 726<br>31 250<br>44 247 |
| (3) | $C_{19}H_{15}N_3O_2$ | Yellow | 317.35 | 154—155 | 71.9/71.7 | 4.8/4.7 | 13.2/13.2 | 317 | 3 318$^a$<br>3 333$^b$ | 7.87$^{d*}$<br>9.89$^e$ | 25 721 |
| (4) | $C_{19}H_{14}N_4O_4$ | Orange | 362.35 | 243—244 | 63.0/63.0 | 3.9/3.8 | 15.5/15.3 | 362 | 3 290$^a$<br>3 285$^b$ | 11.23$^d$<br>11.13$^e$ | 26 320<br>41 670sh |

[a] Nujol mull. [b] $CHCl_3$ solution. [c] $Me_2SO$ solution. [d] $CDCl_3$ solution. [e] $(CD_3)_2SO$ solution with reference to internal tetramethylsilane. [f] $CH_3CN$ solution. * Identified from within aromatic complex multiplet, $\delta_{CH}$ 7.03—8.20.



| | R$^1$ | R$^2$ |
|---|---|---|
| (1) | H | H |
| (2) | $NO_2$ | H |
| (3) | H | $NO_2$ |
| (4) | $NO_2$ | $NO_2$ |

aromatic *cis*-phenyl ring does not impose any severe steric restriction(s). For (**2**) and (**4**) frequency-difference values [$\nu_{NH}$(crystals) – $\nu_{NH}$($CCl_4$)] of 7 and 5 cm$^{-1}$, respectively, indicate very weak NH • • • π interactions in the solid state. In view of the foregoing considerations, variations in $\nu_{NH}$(crystals) of *ca.* 26—30 cm$^{-1}$ between (**2**) and (**4**) as compared with (**1**) and (**3**) highlight the appreciable involvement of the *ortho*-$NO_2$ groups of the former in intramolecular hydrogen bonding. A similar differentiation between (**2**) and (**4**) [with respect to (**1**) and (**3**)] is maintained in solution: $\nu_{NH}$($CHCl_3$) *ca.* 34—48 cm$^{-1}$. In the case of (**2**), where $\nu_{NH}$($Me_2SO$) differs only slightly from both $\nu_{NH}$(crystals) and $\nu_{NH}$($CHCl_3$), it seems likely that the solid-state intramolecular $NO_2$ • • • HN bonded conformation is not seriously disrupted in solution.

$^1$H *N.m.r. Data.*—Both (**2**) and (**4**) show a low-field singlet, $\delta_{NH}$ ~ 11.0, indicative of *ortho*-$NO_2$ group participation in strong intramolecular $NO_2$ • • • HN hydrogen bonding. As expected these signals are solvent independent. For (**1**), which has no such *ortho*-substituent, the NH resonance is much further upfield, and is in fact obscured by the aromatic complex multiplet $\delta_{CH}$ 6.74—7.65 (in $CDCl_3$). In $(CD_3)_2SO$ a singlet is observed at $\delta_{NH}$ 8.76, in agreement with significant solvent participation in intermolecular N–H • • • O=S hydrogen bonding. A similar picture emerges for (**3**): $\delta_{NH}$ 7.87 ($CDCl_3$) is shifted downfield to $\delta_{NH}$ 9.89 [$(CD_3)_2SO$].

*Crystal Structures.*—The structures of compounds (**2**) and (**3**) are illustrated in Figures 1 and 2, which show projections onto the C(1)—C(6) benzene ring plane, together with the atom numbering schemes. There are no significant intermolecular contacts in either structure.

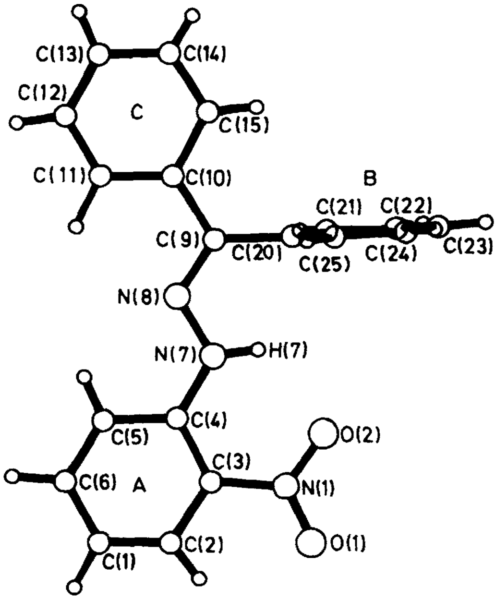


**Figure 1.** Structure of compound (**2**)

The most striking difference between the two structures is in the position of the benzene rings relative to the phenylhydrazone skeleton. For convenience the phenyl rings are denoted A, B, and C.

In (**2**), the angle between ring planes A and B is 83.9°. The remaining part of the molecule, that is rings A and C and the N(7)N(8)C(9) linkage, is approximately planar (angle between A and C is 2.6°). This orientation clearly maximises distances between N(7)–H(7) and ring B. However there are still some short H(7) • • • C contacts. The relevant distances are given in Table 6. Both N(7) and H(7) are approximately equidistant from C(21) and C(25), at mean distances of 3.53 and 2.85 Å respectively, and H(7) is 2.29 Å from C(20). To what extent these distances quantify an NH • • • π interaction is open to question (see later discussion).

In (**3**), as is apparent from Figure 2, the arrangement is very different. The angle between planes A and B is only 52.0°. This means that the NH proton H(7) is 2.43 Å from C(20) and 2.26 Å from C(21), but 3.49 Å from C(25) (see Table 6). The distance from H(7) to the mid-point of C(20)—C(21) is 2.24 Å;

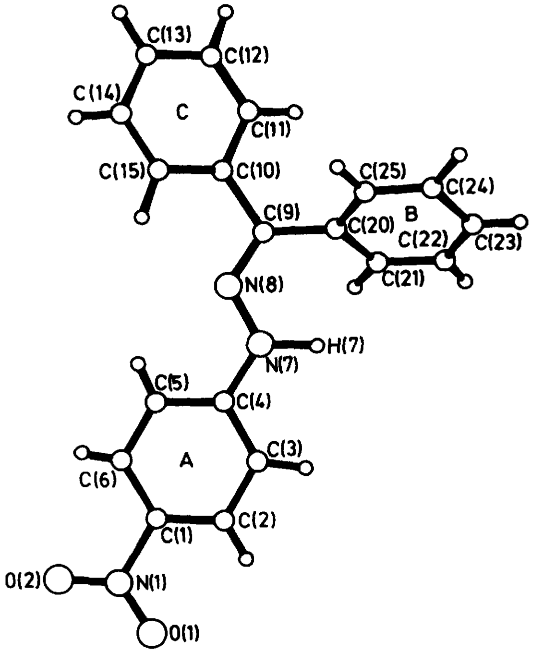


**Figure 2.** Structure of compound (3)

comparison with the van der Waals radii of hydrogen and carbon (1.2 and 1.7 Å) suggests a relatively strong intramolecular NH···π hydrogen bond to the C(20)–C(21) bond. This is to our knowledge the first structure to be reported in which such an N–H···π bond has been demonstrated; moreover these dimensions are comparable with, indeed shorter than, those found for structures which feature O–H···π interactions. For example, in 2,6-diphenylphenol,[5] the hydroxy H atom is 2.43(4) and 2.40(4) Å from two adjacent phenyl carbon atoms. In 2,2-bis-(2-hydroxy-5-methyl-3-t-butylphenyl)-propane, the distances are 2.49 and 2.52 Å,[6] while in 4-nitro-2,6-diphenylphenol the distances are 2.59(3) and 2.48(3) Å.[7]

With regard to OH···π interactions in diphenylphenol systems, the hydroxy hydrogen atom has free rotation around the C–O bond and therefore a position directed towards the aromatic C–C bond is a clear indication of intermolecular hydrogen bonding. Such bonds have OH···carbon distances in the range 2.40—2.59 Å. The geometric requirements of these OH···π (C–C) interactions are stated to be that the O–H bond is roughly parallel to the benzene ring, and that the resulting O–H···midpoint (C–C bond) angle is close to the tetrahedral angle. Certainly these criteria are satisfied in the structures just listed.

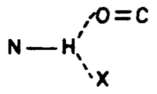
With the NH···π interactions in our phenylhydrazone derivatives of benzophenone there is an immediate contrast. In both (2) and (3), the position of H(7) is fixed by the planarity of the $sp^2$ nitrogen atom N(7), and it is the position of the benzene ring that is adjustable. For (3), H(7)···C(20) and H(7)···C(21) distances are 2.43 and 2.26 Å, and least-squares planes (see Table 7) show that while atoms N(7), N(8), C(9), C(20), and H(7) are approximately coplanar (max. devn. 0.04 Å), the midpoint of C(20)–C(21) is 0.41 Å from the plane, but the N–H···mid-point[C(20)–C(21)] angle is 113°. Thus by all criteria the structure of (3) contains a strong NH···π interaction. The bonding is viewed as resulting from overlap of an occupied π-orbital of the aromatic ring B (HOMO, $e_1$) and the vacant σ* antibonding orbital [LUMO, $\psi_{N(sp^2)} - \psi_{H(1s)}$] associated with the NH group.

The structure of (2) is more difficult to interpret. In this case the NH proton is strongly hydrogen bonded to the *ortho*-NO$_2$ group [N(7)···O(2) 2.89, H(7)···O(2) 2.11(7) Å, N(7)–H(7)···O(2) 123(5)°]. The distances between N(7)–H(7) and ring B (Table 6) suggest an auxiliary weak N–H···π interaction [the i.r. spectrum is equally supportive (see above)] involving two C–C bonds of ring B rather than one, as found in structure (3). Not only is H(7) much closer to C(20) (2.29 Å) than both C(21) (2.91 Å) and C(25) (2.80 Å) but it is only 2.52 and 2.46 Å from the mid-points of the bonds C(20)–C(21) and C(20)–C(25), respectively.

The N–H···mid-point[C(20)–C(21)] and N–H···mid-point [C(20)–C(25)] angles are identical, *viz.* 119°. However, the values of the two H···C(mid-point)···C(20) angles are 63 and 67, respectively [*cf.* 100° in (3)]. We suggest that this geometry represents a weak interaction and indeed an interesting comparison can be found in the structure of 4-nitro-2,6-diphenylphenol.[7] Here the OH proton is not only involved in a strong intramolecular O–H···π(C–C) interaction but is further involved with two carbon atoms of an aromatic ring of a neighbouring molecule with distances of 2.85(2) and 2.89(2) Å, which approach the van der Waals value. Nevertheless the authors of ref. 7 suggest that this represents a weak intermolecular O–H···π (C–C) bonding situation. In (2) the H(7)···C dimensions are similar to these values but with the subtle distinction that the interaction is not just to one C–C bond but to the C(25)–C(20)–C(21) segment of the aromatic ring B.

The bonding picture is one of orbital overlap of a filled π-bonding orbital of the aromatic ring ($e_1$, HOMO) and a directed lone pair on the terminal oxygen ($sp^2$) of the NO$_2$ group (donors) with the empty σ* antibonding orbital [LUMO, $\psi_{N(sp^2)} - \psi_{H(1s)}$] of the NH group (acceptor).

Recently, statistical studies[13,14] of the geometry of the N–H···O=C hydrogen bond suggest that for the three-centre 'bifurcated' system (A), where the NH···O=C contact is the 'major' component and the N–H···X contact (X = O, N, S, or halogen) the 'minor' component of the bond, many of the latter contacts are due to the fortuitous proximity of the proton and the acceptor atom X in the same molecule. Thus as an alternative approach to (2) the disposition of the aromatic ring B can be simply explained on steric grounds, *i.e.* the resulting orientation minimises steric interactions. On balance, however, we believe that there is sufficient evidence for a weak N–H···π[C(25)–C(20)–C(21)] interaction to be postulated. For the bifurcated bond in (2) it seems reasonable that the weakening of the NH···π interaction as minor component [in comparison with the situation in (3), taken as a true representative of such an NH···π interaction] is due to the geometry requirement of the NH···O 'major' component involving the *ortho*-NO$_2$ group. This has the effect of pulling the N(7)–H(7) group away from the π-density of the aromatic ring B to the detriment of effective LUMO–HOMO orbital overlap.



(A)

It is striking that the conformation in (2) is so different from that in (3). The effect of the rotation of plane B relative to plane A is apparent in plane C, which rotates by 25.1° with respect to plane A, thus ensuring an angle of 70.4° with respect to plane B, and thus minimising interplanar contacts.

There are some interesting variations in the other dimensions. For example in both structures the angle N(8)–C(9)–C(20) is much larger than N(8)–C(9)–C(10) [125.2(5) and 114.5(6) in

**(2)**, and 126.1(10) and 114.3(8)° in **(3)**]. This difference has been noted previously, *e.g.* in derivatives of butane-2,3-dione,[15] diethyl 3-oxopentanedioate,[16] and Meldrum's acid,[17] and seems to be a common feature no matter what substituents are bound to C(20). Presumably the non-equivalence is a sensitive reflection of the repulsions involving H(7).

The structure of **(3)** can be compared with structures which possess an oxo group at C(20) which can participate in strong intramolecular N–H $\cdots$ O=C hydrogen bonding, *e.g.* derivatives of Meldrum's acid,[17] dimethyl 2-oxopropanedioate,[18] and dimedone.[19] For these the O $\cdots$ H and O $\cdots$ N distances have mean values of 2.0 and 2.6 Å, respectively, which, conspicuously, are only slightly shorter than the N–H $\cdots$ $\pi$ (C–C) bonds located here. Also for these $\alpha$-oxo group systems, we have noticed a correlation between the geometry of the N(7)–N(8)–C(9) moiety and the C=O $\cdots$ H(7) hydrogen bonding [$o$-$NO_2$ $\cdots$ H(7) hydrogen bonding appears to make little difference to the dimensions]. With such hydrogen bonding present the C(4)–N(7), N(7)–N(8), and N(8)–C(9) bond lengths are 1.40, 1.31, and 1.31 Å, and in the absence of such bonding the values are 1.36, 1.39, and 1.28 Å, respectively. However, the dimensions of **(2)** and **(3)** do not fit ideally into either category and we are unable to draw any conclusions concerning the effect(s) of N–H $\cdots$ $\pi$ (C–C) with respect to N–H $\cdots$ O=C interactions.

It is of interest that in **(3)** the longest of the C–C bonds in the ring B is C(20)–C(21), which is involved in the H interaction. This may be significant.

## Experimental

All solvents were dried over $CaH_2$ and $P_2O_5$ and distilled immediately before use.

The four phenylhydrazones were prepared by treatment of benzophenone (B.D.H.) with the appropriate phenylhydrazine (May and Baker) in the presence of glacial acetic acid–ethanol following the standard procedures.[10] Purification was effected by recrystallisation from $CH_2Cl_2$–light petroleum (b.p. 30—40 °C).

Routine i.r. spectra were obtained using a Perkin-Elmer 580B spectrophotometer with samples either as Nujol mulls sandwiched between CsI plates or in solution contained in CsI cells. $^1H$ N.m.r. spectra were recorded with a Bruker WH90 (90 MHz) spectrometer using tetramethylsilane as internal calibrant in $CDCl_3$ and $(CD_3)_2SO$ solutions. M.p.s were obtained with a Gallenkamp Electrothermal apparatus. Elemental analyses were performed by EMAL Ltd., Beaworthy, Devon. Molecular weight data were determined mass spectrometrically using a Kratos MS80 instrument (electron impact, 70 eV, source temp. 200 °C); the strongest peak in the parent-ion isotope pattern $M^+/z$ was recorded.

**Table 2.** Crystal data

| | (2) | (3) |
|---|---|---|
| Formula | $C_{19}H_{15}N_3O_2$ | $C_{19}H_{14}N_3O_2$ |
| $M$ | 317.35 | 317.35 |
| Crystal class | Monoclinic | Orthorhombic |
| Absences | $h0l$, $h = 2n + 1$ | $hk0$, $k = 2n + 1$<br>$h0l$, $h = 2n + 1$<br>$0kl$, $l = 2n + 1$ |
| Space group | $P2_1/a$ | $Pcab$ |
| $a$/Å | 12.074(5) | 8.468(7) |
| $b$/Å | 12.771(8) | 13.98(1) |
| $c$/Å | 11.998(8) | 26.82(2) |
| $\beta$/° | 118.0(1) | (90) |
| $U$/Å$^3$ | 1 633.5 | 3 175.0 |
| $Z$ | 4 | 8 |
| $F$(000) | 664 | 1 328 |
| $\mu$/cm$^{-1}$ | 0.93 | 0.96 |
| $D_m$/g cm$^{-3}$ | 1.30 | 1.33 |
| $D_c$/g cm$^{-3}$ | 1.29 | 1.32 |
| $\lambda$/Å | 0.7107 | 0.7107 |
| Crystal size (mm) | 0.4 × 0.3 × 0.4 | 0.2 × 0.4 × 0.4 |
| Rotation axis $2\theta_{max.}$ (°) | 50 | 50 |
| No. of independent data | 2 993 | 3 045 |
| No. used in refinement | 1 244 | 1 181 |
| Criterion for data inclusion | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| $R$ | 0.074 | 0.068 |
| $R_w$ | 0.078 | 0.071 |

**Table 3.** Atomic co-ordinates ( × $10^4$) for **(2)** with estimated standard deviations in parentheses

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| C(1) | −2 678(9) | 189(8) | −713(9) |
| C(2) | −1 729(9) | −424(7) | 194(9) |
| C(3) | −534(6) | 15(5) | 1 094(7) |
| C(4) | −331(6) | 1 109(5) | 1 101(7) |
| C(5) | −1 363(7) | 1 714(6) | 187(7) |
| C(6) | −2 513(8) | 1 260(7) | −697(9) |
| N(7) | 828(6) | 1 588(5) | 1 945(6) |
| N(8) | 969(5) | 2 655(4) | 1 877(5) |
| C(9) | 2 095(6) | 3 052(5) | 2 671(7) |
| C(10) | 2 190(6) | 4 218(5) | 2 599(7) |
| C(11) | 1 173(8) | 4 836(6) | 1 730(8) |
| C(12) | 1 281(8) | 5 918(7) | 1 731(9) |
| C(13) | 2 393(9) | 6 423(7) | 2 569(9) |
| C(14) | 3 408(10) | 5 827(8) | 3 390(10) |
| C(15) | 3 338(9) | 4 742(7) | 3 436(10) |
| C(20) | 3 221(6) | 2 416(5) | 3 609(7) |
| C(21) | 4 143(7) | 2 037(6) | 3 341(9) |
| C(22) | 5 164(8) | 1 473(6) | 4 214(10) |
| C(23) | 5 357(7) | 1 274(6) | 5 414(9) |
| C(24) | 4 466(8) | 1 652(8) | 5 686(9) |
| C(25) | 3 409(8) | 2 213(7) | 4 803(8) |
| N(1) | 435(7) | −683(5) | 2 028(8) |
| O(1) | 218(7) | −1 633(5) | 1 916(8) |
| O(2) | 1 468(7) | −324(5) | 2 888(7) |

**Table 4.** Atomic co-ordinates ( × $10^4$) for **(3)** with estimated standard deviations in parentheses

| Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|
| C(1) | −142(10) | 1 318(8) | 2 959(3) |
| C(2) | 384(13) | 2 232(8) | 2 892(4) |
| C(3) | 1 097(12) | 2 473(8) | 2 465(4) |
| C(4) | 1 266(10) | 1 824(7) | 2 083(3) |
| C(5) | 738(11) | 894(7) | 2 162(4) |
| C(6) | 17(10) | 643(7) | 2 597(3) |
| N(7) | 1 912(9) | 2 046(6) | 1 631(3) |
| N(8) | 2 462(9) | 2 946(5) | 1 551(3) |
| C(9) | 3 077(10) | 3 144(7) | 1 123(3) |
| C(10) | 3 588(10) | 4 160(6) | 1 066(3) |
| C(11) | 4 834(11) | 4 394(7) | 749(4) |
| C(12) | 5 385(12) | 5 306(7) | 718(4) |
| C(13) | 4 749(13) | 6 019(8) | 999(4) |
| C(14) | 3 501(12) | 5 794(7) | 1 311(4) |
| C(15) | 2 926(11) | 4 876(7) | 1 348(3) |
| C(20) | 3 237(10) | 2 488(7) | 703(3) |
| C(21) | 3 946(12) | 1 577(7) | 759(4) |
| C(22) | 3 998(11) | 971(9) | 358(5) |
| C(23) | 3 409(13) | 1 235(9) | −90(5) |
| C(24) | 2 789(13) | 2 151(9) | −158(4) |
| C(25) | 2 694(11) | 2 735(7) | 245(4) |
| N(1) | −924(10) | 1 039(8) | 3 442(3) |
| O(1) | −1 328(10) | 207(6) | 3 487(3) |
| O(2) | −1 074(14) | 1 664(7) | 3 753(3) |

**Table 5.** Molecular dimensions of (**2**) and (**3**) (distances in Å, angles in degrees)

| | Structure (**2**) | Structure (**3**) | | Structure (**2**) | Structure (**3**) |
|---|---|---|---|---|---|
| C(1)–C(2) | 1.393(13) | 1.364(14) | C(10)–C(15) | 1.439(11) | 1.375(12) |
| C(1)–N(1) | | 1.506(12) | C(11)–C(12) | 1.387(11) | 1.360(12) |
| C(1)–C(6) | 1.381(12) | 1.361(13) | C(12)–C(13) | 1.401(12) | 1.360(14) |
| C(2)–C(3) | 1.449(11) | 1.338(14) | C(13)–C(14) | 1.385(13) | 1.385(15) |
| C(3)–C(4) | 1.418(10) | 1.376(13) | C(14)–C(15) | 1.390(13) | 1.375(14) |
| C(3)–N(1) | 1.479(10) | | C(20)–C(21) | 1.383(10) | 1.416(13) |
| C(4)–C(5) | 1.439(10) | 1.390(12) | C(20)–C(25) | 1.366(10) | 1.358(13) |
| C(4)–N(7) | 1.424(9) | 1.367(11) | C(21)–C(22) | 1.387(12) | 1.369(14) |
| C(5)–C(6) | 1.416(11) | 1.363(13) | C(22)–C(23) | 1.370(13) | 1.353(16) |
| N(7)–N(8) | 1.379(8) | 1.359(9) | C(23)–C(24) | 1.352(13) | 1.395(15) |
| N(8)–C(9) | 1.341(9) | 1.291(10) | C(24)–C(25) | 1.413(12) | 1.355(14) |
| C(9)–C(10) | 1.499(9) | 1.493(12) | N(1)–O(1) | 1.236(9) | 1.219(11) |
| C(9)–C(20) | 1.529(10) | 1.458(13) | N(1)–O(2) | 1.274(10) | 1.214(11) |
| C(10)–C(11) | 1.420(10) | 1.393(12) | | | |
| | | | | | |
| C(2)–C(1)–C(6) | 119.0(8) | 121.5(9) | C(11)–C(10)–C(15) | 118.1(6) | 118.2(8) |
| C(2)–C(1)–N(1) | | 119.9(9) | C(10)–C(11)–C(12) | 120.3(7) | 121.2(9) |
| C(6)–C(1)–N(1) | | 118.5(9) | C(11)–C(12)–C(13) | 121.1(8) | 121.2(9) |
| C(1)–C(2)–C(3) | 122.1(8) | 119.7(10) | C(12)–C(13)–C(14) | 119.2(7) | 118.1(10) |
| C(2)–C(3)–C(4) | 119.7(7) | 121.2(10) | C(13)–C(14)–C(15) | 121.7(8) | 121.7(9) |
| C(2)–C(3)–N(1) | 119.2(7) | | C(10)–C(15)–C(14) | 119.5(8) | 119.7(9) |
| C(4)–C(3)–N(1) | 121.0(6) | | C(9)–C(20)–C(21) | 123.3(6) | 121.7(9) |
| C(3)–C(4)–C(5) | 116.0(6) | 118.0(9) | C(9)–C(20)–C(26) | 121.7(6) | 120.5(9) |
| C(3)–C(4)–N(7) | 122.5(6) | 123.5(9) | C(21)–C(20)–C(25) | 114.9(7) | 117.8(9) |
| C(5)–C(4)–N(7) | 121.4(6) | 118.4(9) | C(20)–C(21)–C(22) | 122.3(8) | 119.2(10) |
| C(4)–C(5)–C(6) | 123.0(7) | 121.0(9) | C(21)–C(22)–C(23) | 122.8(8) | 121.1(10) |
| C(1)–C(6)–C(5) | 120.0(8) | 118.4(9) | C(22)–C(23)–C(24) | 115.2(8) | 120.2(10) |
| C(4)–N(7)–N(8) | 119.4(6) | 119.1(8) | C(23)–C(24)–C(25) | 122.8(9) | 118.2(10) |
| N(7)–N(8)–C(9) | 116.4(6) | 118.4(9) | C(20)–C(25)–C(24) | 122.0(7) | 123.2(19) |
| N(8)–C(9)–C(10) | 114.5(6) | 114.3(8) | C(3)–N(1)–O(1) | 117.2(8) | |
| N(8)–C(9)–C(20) | 125.2(5) | 126.1(10) | C(3)–N(1)–O(2) | 121.5(6) | |
| C(10)–C(9)–C(20) | 120.3(5) | 119.5(8) | O(1)–N(1)–O(2) | 121.2(7) | 126.2(9) |
| C(9)–C(10)–C(11) | 122.1(6) | 120.4(8) | C(1)–N(1)–O(1) | | 117.1(10) |
| C(9)–C(10)–C(15) | 119.8(6) | 121.2(8) | C(1)–N(1)–O(2) | | 116.7(9) |

**Table 6.** Distances between N(7)–H(7) and benzene ring B* (Å)

| | (**2**) | (**3**) |
|---|---|---|
| N(7)–C(20) | 2.83(1) | 2.80(1) |
| N(7)–C(21) | 3.59(1) | 2.98(1) |
| N(7)–C(25) | 3.47(1) | 3.90(1) |
| H(7)–C(20) | 2.29 | 2.43 |
| H(7)–C(21) | 2.91 | 2.26 |
| H(7)–C(25) | 2.80 | 3.49 |

* Hydrogen atoms in normalised positions (see Experimental section).

**Table 7.** Least-squares planes for (**2**) and (**3**) (distances from planes in Å); values for (**2**) precede those for (**3**)

| | |
|---|---|
| Plane 1 | C(1) −0.02, −0.00, C(2) 0.02, −0.00, C(3) −0.00, 0.01<br>C(4) −0.01, −0.01, C(5) 0.01, 0.01, C(6) 0.00, −0.00 |
| Plane 2 | C(10) 0.01, 0.00, C(11) −0.01, 0.00, C(12) 0.00, −0.00<br>C(13) 0.01, 0.01, C(14) −0.01, −0.00, C(15) −0.00, 0.00 |
| Plane 3 | C(20) −0.00, −0.01, C(21) 0.01, 0.02, C(22) −0.01, 0.00<br>C(23) −0.01, −0.02, C(24) 0.00, 0.02, C(25) 0.00, −0.00 |
| Plane 4 | N(1), O(1), O(2) |

| Angles between planes (°): | | | | | | |
|---|---|---|---|---|---|---|
| | 1 and 2 | 2.6 | 25.1 | 1 and 3 | 83.9 | 52.3 |
| | 1 and 4 | 2.9 | 2.1 | 2 and 3 | 82.5 | 70.4 |

X-*Ray Crystallography*.—Crystals of (**2**) and (**3**) were prepared as already described above. Details of crystal data and the measurement of intensity data are given in Table 2. The crystals were mounted in turn on a Stoe Stadi-2 diffractometer and data were collected *via* variable-width ω scan. Background counts were 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. Both structures were determined by using the MITHRIL package.[20] The hydrogen atoms were first included in calculated positions, but during the final cycles of refinement their parameters were allowed to refine independently. The O, N, and C atoms were refined anisotropically. The refinements were carried out using the full-matrix least-squares method with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$.

In the two structures, the positions of H(7) were normalised in order to correct for systematic errors. This method, suggested by Taylor *et al.*,[14,21] corrects for systematic errors in the *X*-ray results. The treatment involves moving the hydrogen atom positions along the observed N–H bond direction until the N–H distance is equal to 1.030 Å. Calculations were carried out using SHELX76[22] and our own programs on the Amdahl VM370 computer at the University of Reading.

Atomic co-ordinates are given in Tables 3 and 4 and molecular dimensions in Table 5.

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