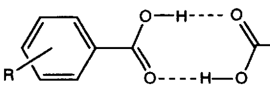
Mixed crystals of pyrazoles and benzoic acids. Part 1. The molecular structure of 3,5-dimethylpyrazole–2,4,6-trimethylbenzoic acid co-crystals

Concepción Foces-Foces,*[a] Lourdes Infantes,[a] Francisco Aguilar-Parrilla,[b] Nicolai S. Golubev,*[b] Hans-Heinrich Limbach[b] and José Elguero[c]

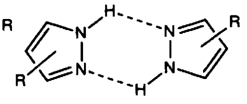
[a] *Departamento de Cristalografía, Instituto de Química Física 'Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain*
[b] *Institut für Organische Chemie (WE 02), Fachbereich Chemie, Freie Universität Berlin, Takustraße 3, D-14195 Berlin, Germany*
[c] *Instituto de Química Médica, CSIC, Juan de la Cierva 3, E-28006 Madrid, Spain*

The title compound 4a has been prepared by slow evaporation of an equimolar mixture of 2,4,6-trimethylbenzoic acid (mesitylenecarboxylic acid) and 3,5-dimethylpyrazole. Two pyrazoles and two benzoic acids form a tetramer unit through N–H ··· O and O–H ··· N hydrogen bonds. The pyrazole rings in 4a show standard geometries. Variable temperature ^{15}N CPMAS NMR experiments showed that no dynamic process takes place in 4a, which is consistent with results of low temperature (77 K) FTIR spectroscopy. This fact can be explained taking into account the acid–base properties of both components.

Proton transfer through **intermolecular** hydrogen bonds seldom occurs in the solid state. The two paradigmatic examples of such processes are benzoic acids, studied by Ernst and co-workers,[1] and NH-pyrazoles studied by ourselves.[2–8] Benzoic acids have been found to form exclusively dimers **1** in the solid state while NH-pyrazoles form dimers **2**, trimers, tetramers and linear polymers (catamers) depending on the *C*-substituents present on the pyrazole ring.



1



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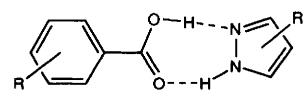
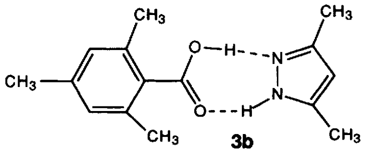


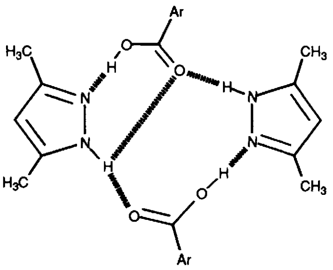
3a



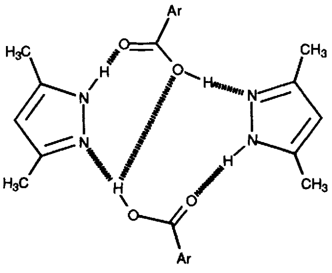
3b

These interesting properties prompted us to mix benzoic acids and NH-pyrazoles in equimolar amounts in the hope of obtaining structures such as **3** where an intermolecular proton transfer between O- and N-atoms could be expected.

Assuming that there are no crystal packing effects, in all these systems the initial and final structures are identical after a double proton transfer has taken place, *i.e.* the proton exchange should be degenerate and characterized by a symmetric double-well potential. The structures differ, however, in the nature of the non-hydrogen atoms involved in the intermolecular hydrogen bond; oxygen in **1**, nitrogen in **2** and both in **3a** and **3b**. The activation energy of the proton transfer increases from oxygen (E_a = 1.14 kcal mol^{-1})[1]† to nitrogen (E_a = 10.6–12.1 kcal mol^{-1})[9] reflecting the increase in distance between the O ··· O (2.64 Å) and N ··· N (2.89 Å, see Table 2). For the case **3a**, where both O–H ··· N and N–H ··· O hydrogen bonds are present, an intermediate value for the activation energy as well as an average intermolecular X–Y ··· Y distance (X, Y = O, N) are expected.



4a



4b

After several attempts of combining benzoic acids and NH-pyrazoles (including the parent compounds, **3a** R = H), co-crystals **4** of 2,4,6-trimethylbenzoic acid (mesitylenecarboxylic acid) and 3,5-dimethylpyrazole were finally obtained. For these co-crystals a structure such as **3b** was expected. 3,5-Dimethylpyrazole was [$^{15}N_2$]-labelled with a view to performing variable temperature ^{15}N solid-state NMR experiments in order to detect a possible proton transfer process.[2,3]

Results and discussion

Molecular structure of compound 4

The geometrical characteristics describing the molecular and crystal structure of compound **4** are supplied in Table 1. Atom

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† 1 cal = 4.184 J.

Table 1 Selected geometrical parameters (Å,°)

N(11)–N(12)	1.347(7)	N(31)–N(32)	1.351(11)
N(11)–C(15)	1.328(10)	N(31)–C(35)	1.327(10)
N(12)–C(13)	1.335(8)	N(32)–C(33)	1.340(8)
C(13)–C(14)	1.388(12)	C(33)–C(34)	1.383(12)
C(14)–C(15)	1.350(11)	C(34)–C(35)	1.383(11)
C(13)–C(16)	1.492(13)	C(33)–C(36)	1.508(13)
C(15)–C(17)	1.519(12)	C(35)–C(37)	1.502(13)
C(21)–C(27)	1.487(19)	C(41)–C(47)	1.486(10)
C(27)–O(21)	1.295(8)	C(47)–O(41)	1.316(8)
C(27)–O(22)	1.216(11)	C(47)–O(42)	1.213(10)
N(12)–N(11)–C(15)	112.3(5)	N(32)–N(31)–C(35)	112.5(6)
N(11)–N(12)–C(13)	104.4(4)	N(31)–N(32)–C(33)	105.3(6)
N(12)–C(13)–C(14)	110.5(6)	N(32)–C(33)–C(34)	109.8(6)
C(13)–C(14)–C(15)	105.8(7)	C(33)–C(34)–C(35)	106.3(7)
C(14)–C(15)–N(11)	107.1(7)	C(34)–C(35)–N(31)	106.1(7)
N(12)–C(13)–C(16)	121.2(7)	N(32)–C(33)–C(36)	121.2(7)
C(14)–C(13)–C(16)	128.4(7)	C(34)–C(33)–C(36)	128.4(7)
N(11)–C(15)–C(17)	121.6(7)	N(31)–C(35)–C(37)	121.6(7)
C(14)–C(15)–C(17)	131.3(7)	C(34)–C(35)–C(37)	131.3(7)
C(26)–C(21)–C(27)	120.9(6)	C(46)–C(41)–C(47)	119.5(6)
C(22)–C(21)–C(27)	118.8(6)	C(42)–C(41)–C(47)	120.5(7)
C(22)–C(21)–C(26)	120.3(6)	C(42)–C(41)–C(46)	119.9(7)
C(21)–C(27)–O(22)	123.1(6)	C(41)–C(47)–O(24)	122.6(6)
C(21)–C(27)–O(21)	115.5(6)	C(41)–C(47)–O(41)	114.9(6)
O(21)–C(27)–O(22)	121.4(7)	O(41)–C(47)–O(42)	122.5(6)
C(22)–C(21)–C(27)–O(21)	115.1(7)	C(42)–C(41)–C(47)–O(41)	119.7(7)
C(22)–C(21)–C(27)–O(22)	−62.8(10)	C(42)–C(41)–C(47)–O(42)	−59.1(10)

Hydrogen interactions

X–H ··· Y	X–H	X ··· Y	H ··· Y	X–H ··· Y
N(11)–H(11) ··· O(22)	0.81(5)	2.923(9)	2.19(5)	151(5)
N(11)–H(11) ··· O(42)	0.81(5)	2.964(9)	2.41(5)	127(4)
N(31)–H(31) ··· O(42)	1.02(8)	2.890(8)	1.89(8)	162(7)
O(21)–H(21) ··· N(32)	1.12(9)	2.608(9)	1.52(9)	161(7)
O(41)–H(41) ··· N(12)	0.98(9)	2,628(9)	1.65(9)	157(7)
C(23)–H(23) ··· O(21)$(-\frac{1}{2} + x, \frac{3}{2} - y, z)$	1.06(5)	3.456(8)	2.41(5)	168(4)
C(34)–H(34) ··· N(12)$(1 + x, y, z)$	0.97(8)	3.422(9)	2.67(8)	135(6)

Table 2 Geometry of X–H ··· Y hydrogen bonds (X, Y = O, N) (between parentheses the standard deviation of the sample)

	X ··· Y	X–H	H ··· Y	X–H ··· Y
Benzoic acids (X = Y = O)	2.642(29)	1.01(12)	1.64(14)	171(7)
NH-Pyrazoles (X = Y = N)	2.894(50)	0.89(11)	2.07(13)	161(15)
Compound **4a** (X = N, Y = O)	2.926(37)	0.88(12)	2.16(26)	147(18)
Compound **4a** (X = O, Y = N)	2.618(14)	1.05(10)	1.58(9)	159(3)

numbering follows the scheme indicated in Fig. 1. The geometry of 3,5-dimethylpyrazole rings shows a similar pattern of bond distances and angles as pyrazole itself.[10] If the geometry of both dimethylpyrazoles in **4** is compared with the ensemble of NH-pyrazoles contained in the Cambridge Structural Database[11] using the so called Paul–Curtin diagrams by plotting differences in bond angles *versus* differences in bond lengths,[12,13] they appear as standard pyrazoles. The only differences concern the C(14)–C(15) and C(34)–C(35) bond lengths. The relative elongation of the latter could be attributed to a C(34)–H(34) ··· N(12) weak interaction while C(14) is not involved in any contact.

As can be seen, the hydrogen bond network is very different from that expected for **3b**. Instead of a dimer, a tetramer **4a** was formed where two pyrazole molecules and two carboxylic acids are linked through O–H ··· N and N–H ··· O hydrogen bonds and with one of the pyrazole NHs involved in an additional hydrogen bond (N–H ··· O, note that all N–H and O–H protons are perfectly localized). The crystal structure consists of these discrete tetramers linked by C–H ··· O=C and C–H ··· N weak interactions. Being a tetramer is not an obstacle to proton transfer in crystals (pyrazole tetramers show four-proton transfer),[3] *e.g.* a four-proton transfer would transform **4a** into **4b**. However, **4a** and **4b** are not identical as regards the additional hydrogen bond; in **4a** it is an N–H ··· O hydrogen bond while in **4b** it would be an O–H ··· O hydrogen bond.

We have now the required information about hydrogen bonds in benzoic acids, NH-pyrazoles and in tetramer **4a** (Table 2) for the following discussion. The data for benzoic acid dimers were obtained from the CSD (October 1994 version, 125 compounds, 134 hits, organic compounds, $R < 0.10$, no errors and no disorder)[11] and that for pyrazoles from our own work (16 compounds, 30 data).[9]

Compound **4a** presents two classes of hydrogen bonds: the N–H ··· O related to the N–H ··· N hydrogen bond present in pyrazoles and the O–H ··· N related to the O–H ··· O bond present in benzoic acids. Thus crystallographically, compound **4a** is not an intermediate case between **1** and **2**, but more a mixed case where the two situations are present.

FTIR spectroscopy

The FTIR spectra of the crystalline compound **4a** in KBr pellets at 77 and 300 K were recorded in the spectral range of 400–4000 cm^{-1} with a spectral resolution of 1 cm^{-1}. The spectra were compared with those of the crystalline 2,4,6-trimethylbenzoic acid (cyclic dimer) and 3,5-dimethylpyrazole (cyclic trimer) measured at 77 K. The frequencies obtained are given in Table 3.

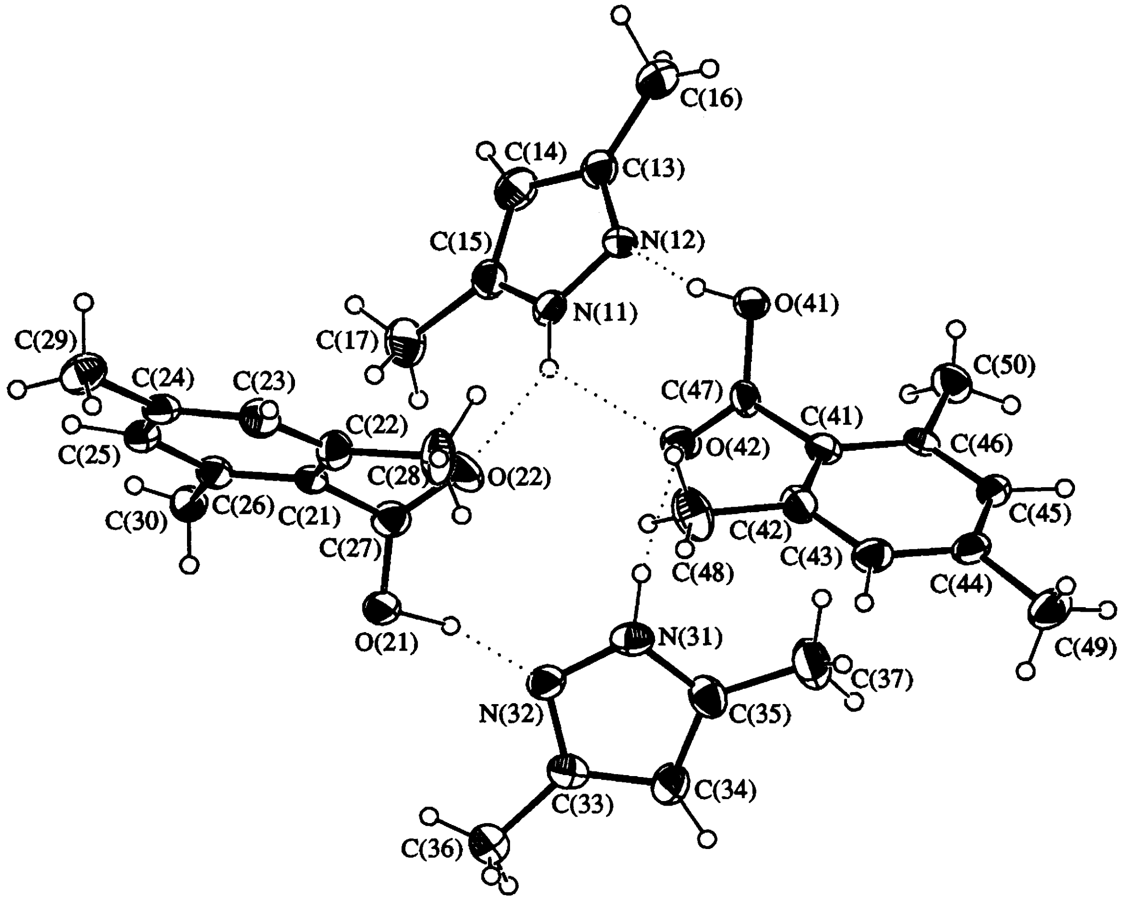

Fig. 1 Ortep[19] view of the title compound showing the atomic numbering. Ellipsoids are drawn at 30% probability level. Dotted lines indicate hydrogen bonds

Table 3 Stretching vibrations (cm^{-1}) for 3,5-dimethylpyrazole, 2,4,6-trimethylbenzoic acid and compound **4a**

Vibration	Cyclic polymers (77 K)	Compound **4a**	
		(77 K)	(300 K)
ν(N–H)	2870^a	3346	3324
		3272	3260
ν(O–H)	2740^a	2480^a	2417^a
ν(C=O)	1683	1675	1684
		1690	1700
ν(C–O)	1292	1294	1285
		1310	1302

^{a} The frequency of the gravity centre of the broad structured band.

It appears that the complex formation results in only slight changes in the frequencies of most vibrational bands of the components, except for several bands related to the groups involved directly in the hydrogen bonds. These are the N–H and O–H bond stretching vibrations as well as the C=O and C–O stretching vibrations. An examination of the frequencies reported in Table 3 leads to the conclusion that the N–H···O hydrogen bonds in compound **4a** are much weaker than the N–H···N bonds in dimethylpyrazole cyclic trimer. The O–H···N hydrogen bonds are stronger than the O–H···O bonds in the acid cyclic dimer. Moreover, this asymmetry gets more pronounced when the temperature decreases: the N–H···O bonds become weaker whereas the O–H···N bonds become stronger. Such an 'anti-co-operativity' effect might prevent the fast multiple proton transfer within the cyclic tetramer.

Note that the doublet splitting of several narrow vibrational bands for compound **4a** could correspond to the non-equivalency of the two sub-units in the tetramer found by X-ray crystallography. However, other explanations, *e.g.* the Fermi resonance, cannot be neglected.

^{15}N VT CPMAS NMR experiments

Experiments were performed at temperatures up to 56 °C, just below the melting point of the compound at 59–63 °C. All recorded spectra showed two sharp lines at 156.4 (-NH-) and 222.8 ppm (-N=). Hence, no signs of proton transfer were observed. This result as well as the values for the -NH- and -N= chemical shifts, which are displaced by 10–15 ppm compared with the values of other studied solid pyrazoles,[14] must be further discussed.

The tetrameric arrangement of the molecules in compound **4a** should not be an obstacle to proton transfer in crystals. Quadruple proton transfers have already been observed for two pyrazole derivatives which form tetramers in the solid state held by N–H···N hydrogen bonds[3,7] and in the case of a pyrazole inclusion compound, where the molecules are held by N–H···O and O–H···N hydrogen bonds.[8] In all these cases, the proton transfer was degenerate and no additional hydrogen bond was formed apart from those involved in the exchange. However, in the case of the studied compound **4**, a quadruple proton transfer would transform **4a** into **4b**, which are not identical structures as regards the additional hydrogen bond, being an N–H···O hydrogen bond in **4a** while in **4b** an O–H···O hydrogen bond would result. The degeneracy of the proton transfer would therefore be disturbed. This asymmetry of complex **4** concerning the hydrogen bond network could lead to the formation of only one tautomer, in this case **4a**, in the solid state.

The ^{15}N chemical shifts of pyrazoles in the solid state often give reliable information about the strength of N–H···N

Table 4 Crystal analysis parameters at 235 K

Crystal data	
Formula	$C_5H_8N_2$, $C_{10}H_{12}O_2$
Crystal habit	Colourless, prism
Crystal size/mm	0.23 × 0.17 × 0.33
Symmetry	Orthorhombic, $Pna2_1$
Unit cell determination:	Least-squares fit from 74 reflections ($\theta < 45°$)
Unit cell dimensions/Å,°	$a = 9.6657(2)$ $b = 13.6047(6)$ $c = 22.5988(13)$ 90, 90, 90
Packing: V/Å^3, Z	2971.7(2), 8
D_c(g cm^{-3}), M, F(000)	1.164, 260.34, 1120
μ/cm^{-1}	5.91
Experimental data	
Technique	Four circle diffractometer: Philips PW1100, bisecting geometry Graphite oriented monochromator: $\omega/2\theta$ scans Detector apertures 1 × 1°. 0.5 min/reflex
Radiation	Cu-Kα
Scan width/°	1.5
θ_{max}/°	65
Number of reflections:	
Independent	2699
Observed	2008 [$3\sigma(I)$ criterion]
Standard reflections:	2 reflections every 90 min 7.5% decay
Solution and refinement	
Solution	Sir92
Refinement:	
Least-Squares on F_o	Full matrix
Parameters:	
Number of variables	502
Degrees of freedom	1506
Ratio of freedom	4.0
Final shift/error	0.17
H atoms	From difference synthesis
Weighting-scheme	Empirical as to give no trends in $\langle \omega\Delta^2F \rangle$ vs. $\langle \lvert F_{obs} \rvert \rangle$ and $\langle \sin\theta/\lambda \rangle$
Max. thermal value/Å^2	$U22[C(37)] = 0.122(8)$
Final ΔF peaks/e Å^{-3}	0.19
Final R and R_w	0.066, 0.065

hydrogen bonds.[14] As stated above, the chemical shift values for the –NH– (156.4 ppm) and –N= (222.8 ppm) atoms in compound **4a** are displaced by *ca.* 10–15 ppm compared with the average values obtained from other solid pyrazole derivatives: 164 (–NH–) and 238 ppm (–N=).[12] This indicates qualitatively that the hydrogen bonds present in compound **4a** must differ from those existing in 'classical' pyrazoles or in pyrazole inclusion compounds. This is in agreement with the crystallographic results of **4a** where additional more or less strong hydrogen bonds were detected affecting the –NH– proton donor site. The chemical shifts observed arise, therefore, from weak N–H···O and O–H···N hydrogen bonds that could be involved in a possible proton transfer. Another example for displaced ^{15}N chemical shift values can be found in the case of 3,5-di-*tert*-butyl-4-nitropyrazole (NH: 155.3, –N=: 241.1 ppm).[14] This compound forms cyclic dimers in the solid state where the –NH– proton is additionally hydrogen bonded to the oxygen atom of the nitro group of another superposed dimer in the unit cell.[6] Here, however, the geometric parameters and larger N–H···O distance of 3.132 Å of the additional hydrogen bond do not affect much the N–H···N bridge, where a proton transfer can take place at high temperature.[15] Since the –N= atoms are not directly affected by the N–H···O hydrogen bond to the nitro group, its ^{15}N chemical shift shows a 'classical' value for pyrazoles.

Conclusions

It is possible to obtain co-crystals of benzoic acid and pyrazole molecules where N–H···O and O–H···N hydrogen bonds are present. However, a fine-tuning of both hydrogen bonds is necessary in order to allow proton transfer since the O–H···N hydrogen bond is usually much stronger than the N–H···O hydrogen bond. Nevertheless, it should be possible to adjust both hydrogen bonds to similar values introducing substituents in both aromatic rings which could modify their acid–base properties, so that proton transfer can take place between oxygen and nitrogen atoms.

Experimental

Both 3,5-dimethylpyrazole and 2,4,6-trimethylbenzoic acid are commercial products. The synthesis of [$^{15}N_2$]3,5-dimethylpyrazole has already been described.[2] From the methanol solution at −18 °C the 1:1 mixture of the two components gives prismatic crystals, *ca.* 0.5 × 1 × 3 mm. The stoichiometry was verified by ^{1}H NMR spectroscopy. The FTIR spectra were recorded on an IFS 66 Bruker instrument.

The ^{15}N CPMAS NMR spectra were recorded on a Bruker CXP 100 spectrometer (FU Berlin) working at 90.02 MHz for protons and 9.12 MHz for ^{15}N. The spectrometer is equipped with a 7 mm CPMAS probehead from Doty Scientific, USA. The spinning speeds were of the order of 2–3 kHz. A Bruker B VT 1000 temperature unit was used to control the temperature of the bearing nitrogen gas stream. The sample temperatures were determined by a 2 × 3 mm platinum resistance thermometer PT-100 from Degussa. It was placed *ca.* 3 mm apart from the coil. The standard CP pulse sequence was performed. General recording parameters: quadrature detection, 5.5 ms ^{1}H 90° pulse width, 2–8 ms CP times, 4 s recycle

Table 5 Final atomic coordinates

Atom	x	y	z	U_{eq}
N(11)	0.1142(5)	0.3632(4)	0.1523(3)	47(2)
N(12)	0.0473(5)	0.3657(4)	0.1000	46(2)
C(13)	−0.0377(7)	0.2887(5)	0.1018(3)	49(2)
C(14)	−0.0213(8)	0.2376(5)	0.1545(4)	57(2)
C(15)	0.0749(7)	0.2877(5)	0.1856(4)	54(2)
C(16)	−0.1340(10)	0.2669(7)	0.0518(5)	78(3)
C(17)	0.1394(10)	0.2679(7)	0.2456(4)	79(3)
C(21)	0.1795(6)	0.5900(4)	0.3120(3)	41(2)
C(22)	0.1155(7)	0.6767(5)	0.2900(4)	52(2)
C(23)	0.0214(7)	0.7243(5)	0.3255(4)	54(2)
C(24)	−0.0171(6)	0.6893(5)	0.3814(3)	47(2)
C(25)	0.0445(6)	0.6023(4)	0.4008(3)	43(2)
C(26)	0.1445(6)	0.5538(4)	0.3677(3)	42(2)
C(27)	0.2855(7)	0.5401(5)	0.2750(4)	48(2)
O(21)	0.4094(5)	0.5390(4)	0.2968(3)	59(2)
O(22)	0.2604(6)	0.5050(5)	0.2268(3)	82(2)
C(28)	0.1486(10)	0.7178(7)	0.2298(4)	78(3)
C(29)	−0.1203(9)	0.7444(6)	0.4184(4)	68(3)
C(30)	0.2115(7)	0.4632(5)	0.3930(4)	53(2)
N(31)	0.5675(5)	0.5121(4)	0.1582(3)	52(2)
N(32)	0.5970(5)	0.5048(4)	0.2162(3)	53(2)
C(33)	0.7354(7)	0.4990(6)	0.2194(4)	54(2)
C(34)	0.7907(7)	0.5040(6)	0.1629(4)	61(2)
C(35)	0.6803(7)	0.5110(6)	0.1245(4)	56(2)
C(36)	0.8071(9)	0.4919(8)	0.2784(4)	82(3)
C(37)	0.6750(10)	0.5143(8)	0.0580(4)	88(4)
C(41)	0.3365(6)	0.6005(5)	0.0091(3)	43(2)
C(42)	0.3751(7)	0.6941(4)	0.0297(4)	48(2)
C(43)	0.4546(7)	0.7544(5)	−0.0061(4)	50(2)
C(44)	0.4953(7)	0.7250(5)	−0.0623(3)	49(2)
C(45)	0.4561(6)	0.6333(5)	−0.0821(3)	43(2)
C(46)	0.3786(6)	0.5692(4)	−0.0479(3)	38(2)
C(47)	0.2613(6)	0.5310(4)	0.0484(3)	41(2)
O(41)	0.1385(4)	0.5041(4)	0.0289(3)	54(1)
O(42)	0.3077(5)	0.5028(4)	0.0950(3)	61(2)
C(48)	0.3328(10)	0.7276(5)	0.0912(4)	73(3)
C(49)	0.5877(7)	0.7887(6)	−0.1006(4)	67(3)
C(50)	0.3432(7)	0.4695(5)	−0.0703(4)	51(2)

delay, spectral width of 7000 Hz. All ^{15}N chemical shifts are related to external solid $^{15}NH_4Cl$ and given with an error of ± 0.3 ppm.

X-Ray structure determination

Crystal data and experimental details are shown in Table 4. The structure was solved by direct methods[16] and refined by a least-squares procedure. Most of the calculations were performed on a VAX6410 computer using the XRAY80 System.[17] The atomic scattering factors were taken from the International Tables for X-Ray Crystallography, vol. IV.[18] Fractional atomic coordinates are given in Table 5. Tables of bond lengths and angles and thermal factors for the non-hydrogen atoms and hydrogen parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

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‡ For details of the CCDC deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, issue 1.