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Intramolecular N—H···O Hydrogen Bonding Assisted by Resonance. III.* Structural Studies of 1-Ketone-2-Arylhydrazone Derivatives

BY VALERIO BERTOLASI, PAOLA GILLI, VALERIA FERRETTI AND GASTONE GILLI

Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy

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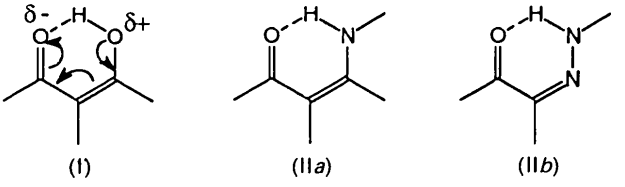
Abstract

The crystal and molecular structures of the following 1-ketone-2-arylhydrazones have been determined: (1) 4-(phenylhydrazono)-3-methyl-4*H*-isoxazol-5-one, $C_{10}H_9N_3O_2$, $M_r = 203.2$, monoclinic, $C2/c$, $a = 11.100$ (3), $b = 7.960$ (2), $c = 21.744$ (4) Å, $\beta = 95.82$ (2)°, $V = 1911.3$ (8) Å^3, $Z = 8$, $D_x = 1.41$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.096$ mm^{-1}, $F(000) = 848$, $T = 295$ K, $R = 0.040$ for 1737 observed reflections; (2) 4-(4-nitrophenylhydrazono)-3-methyl-4*H*-isoxazol-5-one, $C_{10}H_8N_4O_4$, $M_r = 248.2$, monoclinic, $P2_1/c$, $a = 7.046$ (2), $b = 7.774$ (1), $c = 20.917$ (4) Å, $\beta = 98.09$ (2)°, $V = 1134.3$ (4) Å^3, $Z = 4$, $D_x = 1.45$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.108$ mm^{-1}, $F(000) = 512$, $T = 295$ K, $R = 0.048$ for 1599 observed reflections; (3) 4-(2-chlorophenylhydrazono)-3-methyl-4*H*-isoxazol-5-one, $C_{10}H_8ClN_3O_2$, $M_r = 237.6$, orthorhombic, $Pca2_1$, $a = 18.324$ (2), $b = 5.771$ (1), $c = 20.016$ (2) Å, $V = 2116.6$ (6) Å^3, $Z = 8$, $D_x = 1.49$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.345$ mm^{-1}, $F(000) = 976$, $T = 295$ K, $R = 0.044$ for 1359 observed reflections; (4) 4-(4-nitrophenylhydrazono)-3-methyl-1-phenyl-4*H*-pyrazol-5-one, $C_{16}H_{13}N_5O_3$, $M_r = 323.3$, monoclinic, $P2_1/n$, $a = 12.817$ (1), $b = 7.595$ (5), $c = 15.652$ (3) Å, $\beta = 95.74$ (1)°, $V = 1516$ (1) Å^3, $Z = 4$, $D_x = 1.42$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.096$ mm^{-1}, $F(000) = 672$, $T = 295$ K, $R = 0.045$ for 1672 observed reflections. All molecules are planar and present π-delocalization within the ketohydrazone moiety. These conditions should favour the formation of a strong intramolecular N—H···O hydrogen bond assisted by resonance, but in the present case all compounds display hydrogen bonds which can be considered weak or very weak. An analysis of the bond angles suggests that the discrepancy is to be imputed to the fact that the heterocyclic five-membered rings introduce a geometrical constraint which hinders the strengthening of the hydrogen bond. Spectroscopic data, ν(NH) IR frequencies and δ(NH) NMR chemical shifts are in agreement with the hydrogen-bonding magnitude measured by the N···O distances. The steric impossibility of obtaining short N···O distances gives rise to the formation of other intermolecular interactions, relevant to the crystal packing, such as bifurcated N—H···O hydrogen bonds, C—H···O short contacts and π–π interactions.

Introduction

The importance of resonance in determining the strengthening of the intra- and intermolecular hydrogen bonding has been initially assessed for the β-diketone enol systems (I). A synergistic relationship between the shortening of the O—H···O hydrogen bond and the increased delocalization within the π-conjugated chain of single and double bonds connecting the two O atoms has been established and interpreted by means of a semi-empirical model called RAHB (Resonance Assisted Hydrogen Bonding) (Gilli, Bellucci, Ferretti & Bertolasi, 1989; Bertolasi, Gilli, Ferretti & Gilli, 1991; Gilli, Bertolasi, Ferretti & Gilli, 1993). In intramolecularly hydrogen-bonded β-diketone enols, this mechanism may induce the formation of remarkably strong hydrogen bonds having the following features: (i) O···O distances as short as 2.43 Å; (ii) lengthening of the O—H bond to 1.20 Å; (iii) strong or complete delocalization in the heteroconjugated fragment; (iv) lowering of the IR ν(OH) frequency from 3600 to 2560 cm^{-1}; (v) downfield shift of the enolic proton resonance from 5–6 to 17 p.p.m.



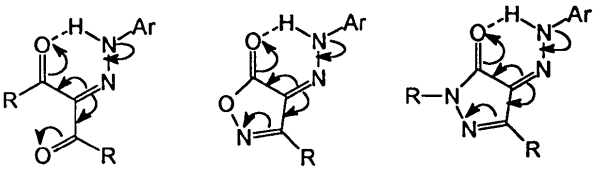
(I) (II*a*) (II*b*)

Intramolecular enaminone (II*a*) and ketohydrazone (II*b*) fragments can give analogous intramolecular hydrogen bonds, which should be assisted by resonance. Crystal-structure data on simple

* The previous paper of this series has been published as part 2 (Bertolasi *et al.*, 1993).

ketohydrazones (II*b*) forming intramolecular hydrogen bonds are not available, but those for enaminones (II*a*) display a π-conjugated system almost totally delocalized and values of N···O distances in the range 2.65–2.68 Å [see for example N···O = 2.653 (8) Å in allyl 1-deoxy-1-[(1-methyl-2-benzoylvinyl)amino]-α-D-fructofuranoside (Diánez, López-Castro & Márquez, 1988) and N···O = 2.681 (2) Å in 1-phenyl-3-(2-hydroxyphenylamino)-2-buten-1-one (Glowiak & Sobczak, 1992)] to be compared with the usually accepted value for intramolecular N···O hydrogen bonds of 2.775 Å (Taylor, Kennard & Versichel, 1984*a*).

Although the π-delocalization observed within the enaminone fragment is in agreement with the expectation, the N···O distance is much less shortened than in the O—H···O case, because *d*(O···O) of 2.43 Å, reported above, would correspond to a N···O distance of *ca* 2.50 Å, in consideration of the differences of bond and van der Waals' radii. It has been recently suggested (Gilli, Bertolasi, Ferretti & Gilli, 1994) that only homonuclear *A*—H···*A* hydrogen bonds (*A* = O, N, F) can become very short, while heteronuclear ones (such as N—H···O) must be relatively longer because of the electronegativity difference of the donor and acceptor atoms. We have recently attempted to identify the chemical substituents able to reduce such electronegativity differences and therefore to shorten the resonance-assisted hydrogen bond. A first class was that of compounds containing the diketohydrazone group. Structural studies (Drew & Willey, 1985; Bertolasi *et al.*, 1993; Bertolasi *et al.*, 1994) on 1,3-diketone-2-arylhydrazones (III) have actually shown that they form strong intramolecular hydrogen bonds as short as 2.55 Å, associated with a significant π-conjugation along the O=C—C=N—NH heterodienic system (particularly in the N—N=C moiety), a lowering of the ν(NH) IR stretching frequency to 3000 cm^{-1} and an increase of the δ(NH) NMR chemical shift up to 15.9 p.p.m. The shortening of the hydrogen bond was interpreted as due to the electron-attracting carbonyl in position 2, which was capable, by resonance, of increasing the positive charge on the N—H nitrogen. Since a similar effect could be expected in compounds of type (IV*a*,*b*), because the imino group is almost equivalent to the carbonyl in (III) as far as resonance within the N—N=C—C=N heterodienic moiety is concerned, the present paper reports the crystal structures and the spectroscopic data for four such compounds, three (IV*a*) containing the isoxazole (*X* = O) and one (IV*b*) the pyrazole (*X* = NR) ring. At the same time, a survey of the crystal structures of some related compound, retrieved from the Cambridge Structural Database (CSD) (Allen *et al.*, 1979), is reported in order to show to what degree the hydrogen bond strength is controlled by π-conjugation along the ketohydrazone moiety or by other electronic or steric factors.



Experimental

The four compounds were synthesized using standard methods (Summers, Freeman & Shields, 1965) and recrystallized from mixtures of benzene/ethyl acetate. Crystal data, data collection and refinement details are given in Table 1.* All X-ray diffraction data were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromoted Mo $K\alpha$ radiation (λ = 0.71069 Å) with an $\omega/2\theta$ scan technique. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections in the range $10 < \theta < 15°$. Intensities of three standard reflections were measured every 2 h and did not show significant variations for any of the four compounds investigated. All intensities were corrected for Lorentz and polarization. Scattering factors were taken from Cromer & Waber (1974). The structures were solved by direct methods using the *SIR*88 (Burla *et al.*, 1989) system of programs and all other calculations were accomplished using *MolEN* (Fair, 1990) and *PARST* (Nardelli, 1983). All structures were refined by full-matrix least squares except (3), which was refined in two blocks, one for each independent molecule. The refinement was carried out on *F* with anisotropic non-H atoms and isotropic H atoms. All H-atom positions were determined from the ΔF synthesis calculated after the first cycles of isotropic refinement. Systematic extinctions of (3) were compatible with both $Pca2_1$ and *Pcam* space groups, with *Z* = 8. Direct methods failed to find a solution in *Pcam* and the crystal structure was solved and refined in the space group $Pca2_1$. After the refinement it was evident that its asymmetric unit consists of two molecules related by a non-crystallographic centre of symmetry, which, however, is not in a position compatible with the higher symmetry space group *Pcam*. The significant differences in bond distances and angles between the two indepen-

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA0053) Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data and summary of experimental details for* (1)–(4)

	(1)	(2)	(3)	(4)
Formula	$C_{10}H_9N_3O_2$	$C_{10}H_8N_4O_4$	$C_{10}H_8ClN_3O_2$	$C_{16}H_{13}N_5O_3$
M_r	203.2	248.2	237.6	323.3
Space group	$C2/c$	$P2_1/c$	$Pca2_1$	$P2_1/n$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a (Å)	11.100 (3)	7.046 (2)	18.324 (2)	12.817 (1)
b (Å)	7.960 (2)	7.774 (1)	5.771 (1)	7.595 (5)
c (Å)	21.744 (4)	20.917 (4)	20.016 (2)	15.652 (3)
β (°)	95.82 (2)	98.09 (2)		95.74 (1)
V (Å^3)	1911.3 (8)	1134.3 (4)	2116.6 (6)	1516 (1)
Z	8	4	8	4
D_x (Mg m^{-3})	1.41	1.45	1.49	1.42
$F(000)$	848	512	976	672
μ (Mo $K\alpha$) (mm^{-1})	0.096	0.108	0.345	0.096
Crystal size (mm^3)	0.12 × 0.21 × 0.48	0.17 × 0.38 × 0.43	0.07 × 0.17 × 0.48	0.10 × 0.14 × 0.55
Measured reflections	2915	3369	2633	3767
Independent reflections	2785	3287	2633	3704
R_{int}	0.10	0.006	—	0.017
No. of observed reflections, N_o	1737 [$I > 3\sigma(I)$]	1599 [$I > 3\sigma(I)$]	1359 [$I > 2\sigma(I)$]	1672 [$I > 3\sigma(I)$]
θ_{min}–θ_{max} (°)	2–30	2–30	2–30	2–28
hkl range	0,15; 0,11; −30,30	−9,9; 0,10; 0,29	0,24; 0,7; 0,26	−16,16; 0,10; 0,20
R*	0.040	0.048	0.044	0.045
wR†	0.050	0.059	0.042	0.050
p‡	0.03	0.05	0.03	0.04
N_o/N_v	10.1	8.1	7.7	6.2
Max. shift/e.s.d.	0.03	0.03	0.05	0.02
No. of variables (N_v) (last cycle)	172	196	177	269
GOF§	1.84	1.63	1.32	1.48
Largest ΔF peak (e Å^{-3})	0.11	0.18	0.23	0.17

* $R = \sum|\Delta F|/\sum|F_o|$.
† $wR = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$.
‡ $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$.
§ GOF = $[\sum|\Delta F|^2/(N_o - N_v)]^{1/2}$.

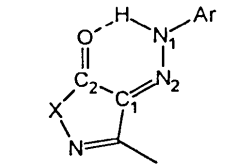
dent molecules cannot be imputed to a wrong space-group choice, but to differences of crystal environment, as discussed below.

IR spectra were recorded on a Nicolet 510P-FTIR spectrometer from KBr pellets and ^{1}H NMR spectra in a solution of $CDCl_3$ on a Gemini 300 Varian spectrometer.

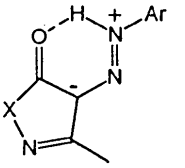
Results and discussion

Final coordinates are given in Table 2 and a selection of bond distances, bond angles and torsion angles in Table 3. *ORTEP* (Johnson, 1976) views of the molecules, projected on the mean hydrazone plane, are shown in Figs. 1–4 together with their unit-cell contents. Torsion angle values (Table 3) show that all molecules are approximately planar, displaying Z configuration around the C(1)=N(2) double bond and *antiperiplanar* conformation of the arylhydrazone group: this arrangement allows the formation of an intramolecular N—H···O hydrogen bonding closing a chelate six-membered conjugated ring. The corresponding hydrogen-bonding parameters are given in Table 4.

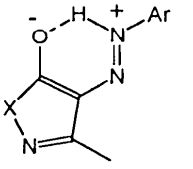
The pattern of bond distances within the heterodienic system can be accounted for in terms of the contributions of the main polar forms (V*b–d*) to the ground state of the molecule, which have been calculated by means of the Pauling's (1947) bond-order formula using standard pure single and double bond distances in planar systems of d(N—N) = 1.401, d(N=N) = 1.240, d(C—N) = 1.410, d(C=N) = 1.279, d(C—C) = 1.500, d(C=C) = 1.331, d(C—O) = 1.380 and d(C=O) = 1.200 Å derived from Allen *et al.* (1987). These contributions are, on average, 10, 10 and 25% for forms (V*b*), (V*c*) and (V*d*), respectively. Because C(1)=N(2) and N(1)—N(2) bond variations are involved in all three resonance forms, the overall delocalization in the fragment has been evaluated by means of an empirical parameter, Λ,



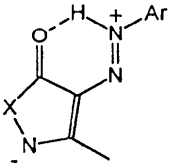
X = O, N—R (V*a*)



(V*b*)



(V*c*)



(V*d*)

Table 2. *Atomic coordinates and equivalent isotropic parameters with e.s.d.'s in parentheses*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B (Å^2)
(1) 4-(Phenylhydrazono)-3-methyl-4*H*-isoxazol-5-one				
O(1)	0.3088 (1)	−0.2043 (1)	0.56158 (5)	4.53 (2)
O(2)	0.2996 (1)	−0.1615 (1)	0.66354 (5)	4.29 (2)
N(1)	0.1568 (1)	0.0551 (2)	0.49782 (5)	3.01 (2)
N(2)	0.1431 (1)	0.1072 (2)	0.55368 (5)	2.83 (2)
N(3)	0.2413 (1)	−0.0339 (2)	0.70150 (6)	3.96 (3)
C(1)	0.1941 (1)	0.0230 (2)	0.60109 (6)	2.67 (2)
C(2)	0.2710 (1)	−0.1238 (2)	0.60263 (7)	3.24 (3)
C(3)	0.1820 (1)	0.0636 (2)	0.66438 (6)	2.94 (3)
C(4)	0.1121 (2)	0.2036 (2)	0.68743 (7)	4.13 (3)
C(5)	0.1028 (1)	0.1470 (2)	0.44672 (6)	2.75 (2)
C(6)	0.1259 (1)	0.0970 (2)	0.38803 (6)	3.21 (3)
C(7)	0.0741 (2)	0.1852 (2)	0.33724 (6)	3.78 (3)
C(8)	0.0007 (2)	0.3209 (2)	0.34450 (7)	4.06 (3)
C(9)	−0.0216 (1)	0.3694 (2)	0.40304 (7)	3.96 (3)
C(10)	0.0287 (1)	0.2834 (2)	0.45479 (6)	3.35 (3)
H(1)	0.201 (1)	−0.050 (2)	0.4915 (8)	5.9 (4)*
(2) 4-(4-Nitrophenylhydrazono)-3-methyl-4*H*-isoxazol-5-one				
O(1)	0.5481 (2)	0.0464 (2)	0.06732 (7)	4.98 (4)
O(2)	0.6101 (3)	0.0872 (2)	0.17481 (7)	5.57 (4)
O(3)	0.9181 (3)	−0.9764 (2)	−0.08739 (8)	6.14 (4)
O(4)	0.7888 (3)	−0.8380 (2)	−0.17088 (8)	7.17 (5)
N(1)	0.6860 (2)	−0.2916 (2)	0.04094 (7)	3.30 (3)
N(2)	0.7294 (2)	−0.3022 (2)	0.10415 (7)	3.44 (3)
N(3)	0.6910 (3)	−0.0190 (3)	0.23091 (9)	5.84 (5)
N(4)	0.8377 (3)	−0.8494 (2)	−0.11302 (9)	4.30 (4)
C(1)	0.6942 (3)	−0.1715 (2)	0.13967 (9)	3.39 (4)
C(2)	0.6102 (3)	−0.0064 (3)	0.12038 (9)	3.80 (4)
C(3)	0.7374 (3)	−0.1652 (3)	0.20900 (10)	4.46 (5)
C(4)	0.8225 (5)	−0.3033 (4)	0.25230 (10)	7.59 (8)
C(5)	0.7245 (3)	−0.4335 (2)	0.00331 (9)	2.99 (4)
C(6)	0.6914 (3)	−0.4170 (2)	−0.06372 (9)	3.45 (4)
C(7)	0.7275 (3)	−0.5541 (3)	−0.10182 (9)	3.54 (4)
C(8)	0.7974 (3)	−0.7041 (2)	−0.07271 (9)	3.29 (4)
C(9)	0.8312 (3)	−0.7223 (2)	−0.00647 (9)	3.50 (4)
C(10)	0.7933 (3)	−0.5865 (2)	0.03197 (9)	3.34 (4)
H(1)	0.634 (2)	−0.196 (2)	0.0226 (8)	3.3 (4)*
(3) 4-(2-Chlorophenylhydrazono)-3-methyl-4*H*-isoxazol-5-one				
Cl(1*A*)	0.2628 (1)	−0.4807 (3)	0	4.92 (3)
O(1*A*)	0.1978 (2)	0.3520 (7)	0.3126 (2)	5.0 (1)
O(2*A*)	0.2839 (2)	0.6274 (6)	0.3000 (2)	4.40 (8)
N(1*A*)	0.2113 (2)	0.0480 (7)	0.2009 (2)	3.38 (9)
N(2*A*)	0.2696 (2)	0.1701 (7)	0.1840 (2)	3.20 (9)
N(3*A*)	0.3450 (3)	0.6710 (7)	0.2550 (2)	4.3 (1)
C(1*A*)	0.2860 (3)	0.3490 (8)	0.2224 (4)	2.9 (1)
C(2*A*)	0.2501 (3)	0.4241 (8)	0.2815 (3)	3.9 (1)
C(3*A*)	0.3449 (2)	0.5084 (8)	0.2101 (2)	2.68 (9)
C(4*A*)	0.4020 (3)	0.4983 (10)	0.1550 (3)	4.3 (1)
C(5*A*)	0.1939 (3)	−0.1451 (8)	0.1612 (2)	3.1 (1)
C(6*A*)	0.1346 (3)	−0.2794 (9)	0.1811 (3)	3.5 (1)
C(7*A*)	0.1177 (3)	−0.4725 (10)	0.1450 (3)	4.3 (1)
C(8*A*)	0.1559 (3)	−0.5385 (9)	0.0874 (3)	4.0 (1)
C(9*A*)	0.2117 (3)	−0.4021 (9)	0.0692 (3)	3.4 (1)
C(10*A*)	0.2327 (3)	−0.2041 (8)	0.1037 (3)	3.1 (1)
H(1*A*)	0.178 (3)	0.091 (9)	0.236 (2)	6 (1)*
Cl(1*B*)	−0.0092 (1)	0.9857 (3)	0.5799 (1)	5.20 (3)
O(1*B*)	0.0493 (2)	0.1596 (7)	0.2649 (2)	4.77 (9)
O(2*B*)	−0.0366 (2)	−0.1153 (7)	0.2764 (2)	4.72 (9)
N(1*B*)	0.0351 (2)	0.4642 (7)	0.3786 (2)	3.35 (9)
N(2*B*)	−0.0204 (2)	0.3347 (7)	0.3936 (2)	2.89 (8)
N(3*B*)	−0.0953 (2)	−0.1650 (7)	0.3252 (2)	4.3 (1)
C(1*B*)	−0.0367 (3)	0.1597 (8)	0.3563 (2)	2.8 (1)
C(2*B*)	−0.0009 (3)	0.0750 (9)	0.2954 (3)	3.6 (1)
C(3*B*)	−0.0924 (3)	−0.0026 (9)	0.3671 (3)	4.0 (1)
C(4*B*)	−0.1437 (4)	0.0065 (13)	0.4210 (3)	5.7 (2)
C(5*B*)	0.0563 (3)	0.6571 (8)	0.4157 (2)	2.9 (1)
C(6*B*)	0.1133 (3)	0.7963 (9)	0.3940 (2)	3.5 (1)
C(7*B*)	0.1337 (3)	0.9882 (9)	0.4305 (3)	3.5 (1)
C(8*B*)	0.0947 (3)	1.0412 (8)	0.4863 (2)	2.9 (1)
C(9*B*)	0.0386 (3)	0.9050 (11)	0.5084 (2)	3.3 (1)
C(10*B*)	0.0186 (3)	0.7106 (8)	0.4740 (2)	3.1 (1)
H(1*B*)	0.054 (2)	0.432 (6)	0.346 (2)	1.1 (8)*
(4) 4-(4-Nitrophenylhydrazono)-3-methyl-1-phenyl-4*H*-pyrazol-5-one				
O(1)	0.8626 (1)	0.3410 (3)	−0.0579 (1)	4.18 (4)
O(2)	0.8343 (2)	−0.1832 (4)	0.4295 (1)	6.66 (6)
O(3)	1.0025 (2)	−0.1838 (3)	0.4536 (1)	6.30 (6)
N(1)	0.9484 (2)	0.1706 (3)	0.0902 (1)	3.44 (4)
N(2)	1.0399 (2)	0.1821 (3)	0.0586 (1)	3.46 (4)
N(3)	1.1120 (2)	0.3734 (3)	−0.1296 (1)	3.84 (5)
N(4)	1.0026 (1)	0.4050 (3)	−0.1383 (1)	3.27 (4)
N(5)	0.9216 (2)	−0.1482 (3)	0.4090 (1)	4.43 (5)
C(1)	1.0421 (2)	0.2604 (3)	−0.0154 (1)	3.12 (5)
C(2)	0.9556 (2)	0.3377 (3)	−0.0704 (2)	3.04 (5)
C(3)	1.1345 (2)	0.2899 (4)	−0.0581 (2)	3.68 (6)
C(4)	1.2438 (2)	0.2392 (5)	−0.0269 (2)	6.14 (8)
C(5)	0.9426 (2)	0.0912 (3)	0.1700 (2)	3.06 (5)
C(6)	0.8469 (2)	0.0819 (4)	0.2032 (2)	3.76 (6)
C(7)	0.8395 (2)	0.0028 (4)	0.2816 (2)	3.73 (6)
C(8)	0.9288 (2)	−0.0632 (3)	0.3262 (2)	3.35 (5)
C(9)	1.0249 (2)	−0.0521 (4)	0.2948 (2)	3.83 (6)
C(10)	1.0319 (2)	0.0237 (4)	0.2161 (2)	3.55 (6)
C(11)	0.9566 (2)	0.4862 (3)	−0.2150 (2)	3.29 (5)
C(12)	1.0153 (2)	0.5082 (4)	−0.2838 (2)	3.98 (6)
C(13)	0.9705 (2)	0.5867 (4)	−0.3582 (2)	4.82 (7)
C(14)	0.8688 (2)	0.6437 (4)	−0.3642 (2)	5.10 (7)
C(15)	0.8109 (2)	0.6238 (4)	−0.2955 (2)	4.98 (7)
C(16)	0.8541 (2)	0.5452 (4)	−0.2203 (2)	4.12 (6)
H(1)	0.893 (2)	0.220 (3)	0.060 (1)	3.8 (5)*

* Refined isotropically.

derived from these bond distances. It is defined as $\Lambda = [1 + q/Q]/2$, where q is the difference d[N(1)—N(2)] − d[N(2)═C(1)] between the actual distances and Q is the same difference between the standard values. Λ is calculated to be 0.484 for a complete π-delocalization, while systems with pure double and single bonds assume the values of 1 or 0.029 for the C═N—N and C—N═N situations, respectively. The range of values observed, $0.49 \le \Lambda \le 0.56$, is indicative of a good degree of π-delocalization. Data relevant to the discussion of these differences are summarized in Table 5, which reports the values of d(N···O), Λ, δ(NH), ν(NH) and the internal angles of the hydrogen-bonded ring for the present ketohydrazones fused with the isoxasole ring (1–3: Class 1) and with the pyrazole ring (4 and four more compounds taken from the CSD files: Class 2). The same data for diketohydrazones (Class 3), averaged from 11 different molecules, are also reported.

Although in all these compounds the π-delocalization in the ketohydrazone moiety and its planarity are favourable conditions for the formation of a strong hydrogen bond assisted by resonance, the observed N···O distances indicate that this happens only for diketohydrazones [Class 3: average d(N···O) = 2.58 (2) Å], but not for ketohydrazones containing both isoxazole [Class 1: average d(N···O) = 2.89 (3) Å] and pyrazole rings [Class 2: average d(N···O) = 2.76 (3) Å]. Both NMR and IR data

Table 3. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *with e.s.d.'s in parentheses*

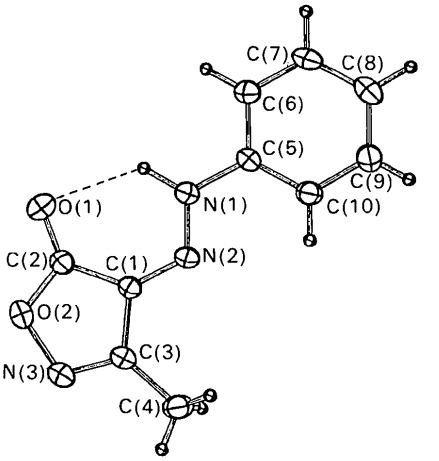
		(1)	(2)	(3A)	(3B)	(4)
N(1)—N(2)		1.307 (2)	1.317 (2)	1.324 (5)	1.297 (5)	1.320 (4)
N(1)—C(5)		1.412 (2)	1.404 (2)	1.405 (6)	1.393 (6)	1.396 (4)
N(2)—C(1)		1.309 (2)	1.303 (2)	1.322 (6)	1.291 (6)	1.305 (3)
C(1)—C(2)		1.446 (2)	1.447 (3)	1.421 (7)	1.468 (7)	1.457 (3)
C(1)—C(3)		1.433 (2)	1.440 (3)	1.439 (7)	1.402 (7)	1.434 (4)
C(2)—O(1)		1.208 (2)	1.206 (2)	1.216 (7)	1.207 (7)	1.227 (3)
C(2)—O(2)		1.364 (2)	1.351 (2)	1.377 (7)	1.334 (7)	
C(2)—N(4)						1.372 (3)
N(3)—O(2)		1.465 (2)	1.482 (2)	1.459 (6)	1.481 (5)	
N(3)—N(4)						1.416 (3)
C(3)—N(3)		1.287 (2)	1.285 (3)	1.299 (6)	1.259 (7)	1.294 (4)
C(5)—N(1)—N(2)		119.1 (1)	118.6 (2)	117.4 (4)	123.7 (4)	119.5 (2)
N(1)—N(2)—C(1)	θ_3	119.2 (1)	119.2 (2)	116.8 (4)	119.9 (4)	117.5 (2)
N(2)—C(1)—C(2)	θ_2	129.7 (1)	129.5 (2)	128.1 (5)	129.6 (5)	128.7 (2)
C(1)—C(2)—O(1)	θ_1	131.3 (2)	129.8 (2)	133.4 (5)	128.7 (5)	127.4 (2)
N(2)—C(1)—C(3)		124.4 (1)	124.8 (2)	124.8 (4)	127.0 (4)	125.2 (2)
O(1)—C(2)—O(2)		122.5 (1)	123.3 (2)	120.5 (5)	124.2 (5)	
O(1)—C(2)—N(4)						128.7 (2)
O(1)—C(2)—C(1)—N(2)		1.0 (3)	2.6 (4)	0.5 (8)	−4.7 (9)	−1.4 (5)
C(3)—C(1)—N(2)—N(1)		−177.5 (2)	−178.9 (2)	−176.7 (4)	176.8 (5)	177.9 (2)
C(1)—N(2)—N(1)—C(5)		−179.4 (1)	−179.9 (2)	−178.9 (4)	179.5 (4)	−178.7 (2)
N(2)—N(1)—C(5)—C(6)		175.2 (1)	−175.4 (2)	177.0 (4)	−175.6 (4)	179.1 (3)
N(2)—N(1)—C(5)—C(10)		−4.8 (2)	4.8 (3)	−3.6 (7)	3.1 (7)	−0.3 (4)

Table 4. *Hydrogen-bonding parameters* (Å, °) *and short* C—H···O *contacts with e.s.d.'s in parentheses*

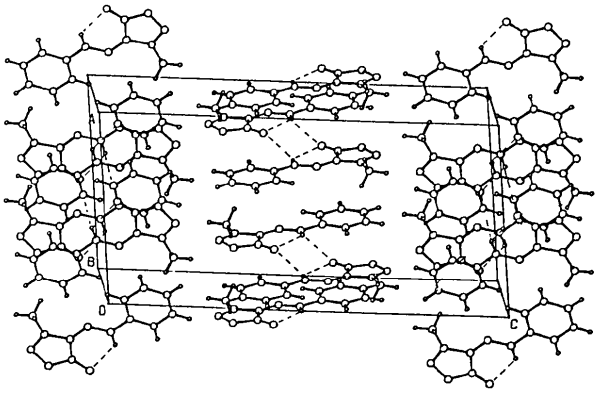
	D—H	*D*···*A*	H···*A*	*D*—H···*A*
(1)				
N(1)—H(1)···O(1')	0.99 (2)	2.925 (2)	2.21 (2)	128 (1)
N(1)—H(1)···O(1'')	0.99 (2)	3.116 (2)	2.27 (2)	143 (1)
C(6)—H(6)···O(1'')	0.94 (2)	3.367 (2)	2.67 (2)	131 (1)
(2)				
N(1)—H(1)···O(1')	0.89 (2)	2.882 (2)	2.22 (2)	130 (1)
N(1)—H(1)···O(1''')	0.89 (2)	3.230 (2)	2.42 (2)	151 (1)
C(6)—H(6)···O(1''')	0.97 (2)	3.334 (2)	2.47 (2)	148 (2)
(3)				
N(1*A*)—H(1*A*)···O(1*A*')	0.96 (5)	2.853 (6)	2.18 (5)	126 (4)
N(1*A*)—H(1*A*)···O(1*B*')	0.96 (5)	3.297 (5)	2.46 (5)	145 (3)
C(6*A*)—H(6*A*)···O(1*B*')	1.00 (4)	3.417 (7)	2.64 (4)	133 (3)
N(1*B*)—H(1*B*)···O(1*B*')	0.76 (4)	2.887 (6)	2.26 (4)	140 (4)
N(1*B*)—H(1*B*)···O(1*A*')	0.76 (4)	3.325 (5)	2.76 (4)	133 (4)
C(6*B*)—H(6*B*)···O(1*A*')	1.09 (4)	3.410 (6)	2.48 (4)	142 (3)
(4)				
N(1)—H(1)···O(1')	0.90 (2)	2.783 (3)	2.06 (2)	137 (2)

Symmetry codes: (i) x, y, z; (ii) $\frac{1}{2}-x, -\frac{1}{2}-y, 1-z$; (iii) $1-x, -y, -z$.

[δ(NH) proton chemical shifts and ν(NH) stretching frequencies] are in perfect agreement with the values of the N···O contact distances, longer bonds showing smaller chemical shifts and higher IR frequencies. An analysis of the bond angles suggests that these differences are to be imputed to the fact that the heterocyclic five-membered rings introduce a geometrical constraint which hinders the shortening of the hydrogen bond. In Class 3, where there are no constraints, θ_1 (O=C—C angle) is 119° and θ_2 (C—C=N angle) is 122°, on average (Table 5). In Classes 1 and 2, these angles are $\theta_1 = 131$ and 128° and $\theta_2 = 129$ and 128°, respectively, and, therefore, too large to allow the strengthening of the hydrogen



(*a*)



(*b*)

Fig. 1. (*a*) *ORTEP* (Johnson, 1976) view and atom numbering for (1). The thermal ellipsoids are drawn at the 30% probability level. (*b*) Unit cell and its contents.

bond. This interpretation is supported by the value of θ_3 (C=N—N angle): this is as wide as 121° in Class 3, where the shortening of the intramolecular hydrogen bond is also made possible by the shrinking of θ_1 and θ_2, while in compounds of Classes 1 and 2, where θ_1 and θ_2 are essentially blocked, θ_3 turns out to be contracted in consequence of the hydrogen-bond attraction force to 119 and 117°, respectively.

The impossibility of establishing a short N···O distance, because of steric strain, leaves on the O and H atoms residual capacities to give rise to the formation of other intermolecular interactions relevant to the crystal packing. Accordingly, the O(1) oxygen and the N(1)—H hydrogen of (1–3), besides forming the intramolecular hydrogen bond, are implied in bifurcated intermolecular interactions which couple the molecules around a centre or a 'pseudo-centre' of symmetry, as shown, for example, for (1) in Fig. 5. In addition, these dimers are stabilized by further short intermolecular C—H···O contacts (Table 4). It is worthy to note that neither (4) and its analogues of Class 1 nor diketohydrazones of Class 3, which all present shorter intramolecular hydrogen bonds, form these intermolecular interactions. This is in agreement with the suggestion (Taylor, Kennard & Versichel, 1984*b*) that a bifurcated hydrogen bond requires the previous formation of another weak hydrogen bond, where the partial negative charge present on the acceptor atom is not completely saturated by the partial positive charge on the donor group. In addition to these intramolecular and intermolecular hydrogen bonds, the molecules are packed in the

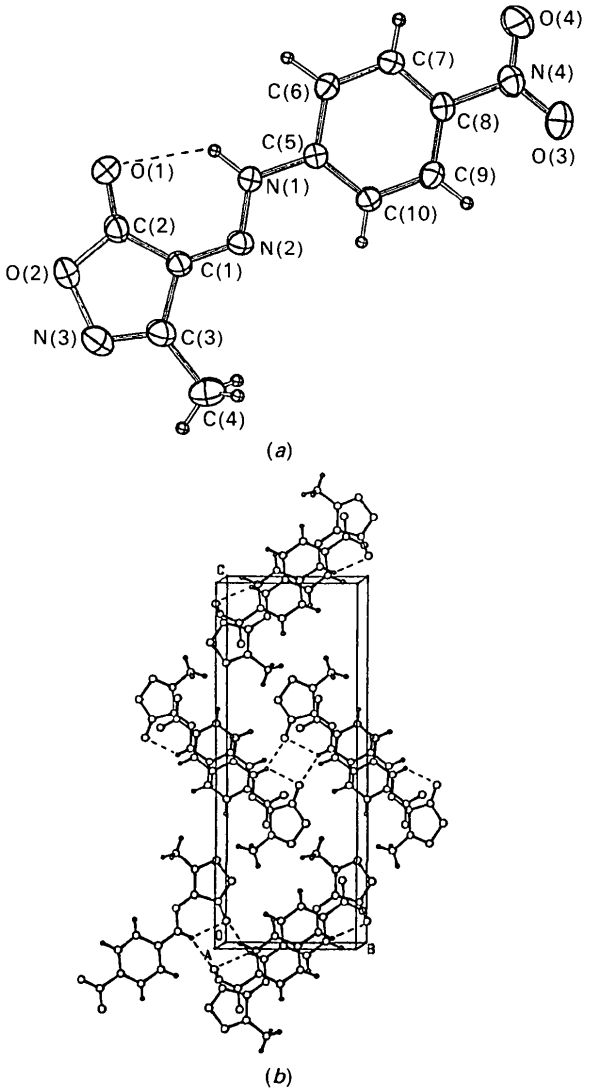


Fig. 2. (*a*) *ORTEP* (Johnson, 1976) view and atom numbering for (2). The thermal ellipsoids are drawn at the 30% probability level. (*b*) Unit cell and its contents.

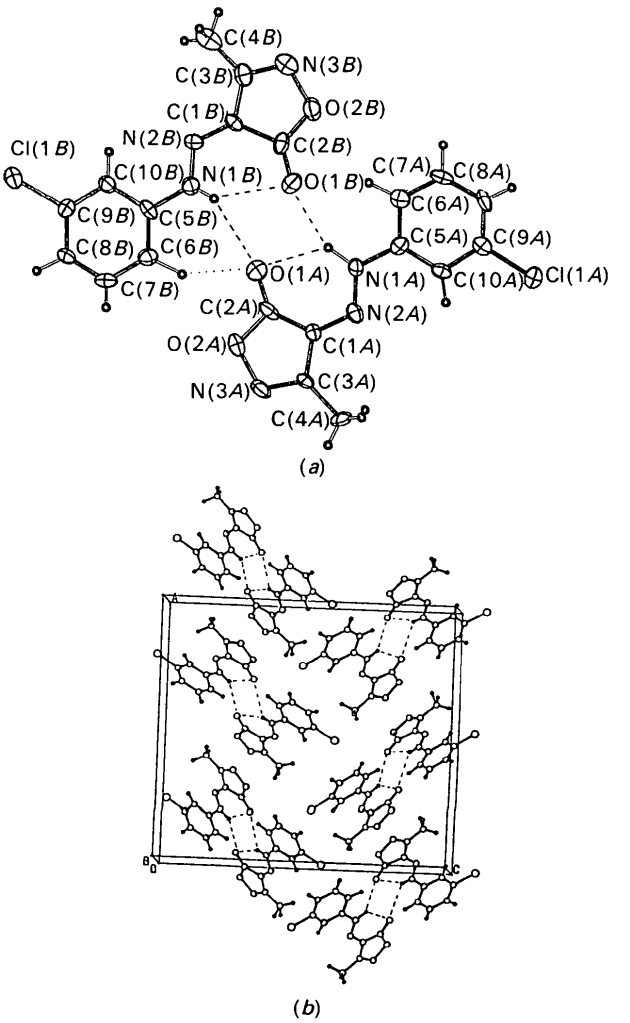
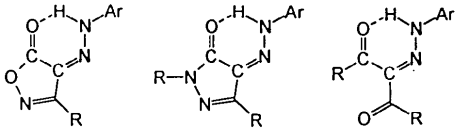


Fig. 3. (*a*) *ORTEP* (Johnson, 1976) view and atom numbering for the two independent molecules of (3). The thermal ellipsoids are drawn at the 30% probability level. (*b*) Unit cell and its contents.

Table 5. *Summary of structural and spectroscopic data for compounds containing the ketohydrazone or diketohydrazone fragment*

Refcode refers to the code of the compound in the CSD file; Λ is defined in the text; ν(NH) measured in KBr pellets; δ(NH) measured in $CDCl_3$.



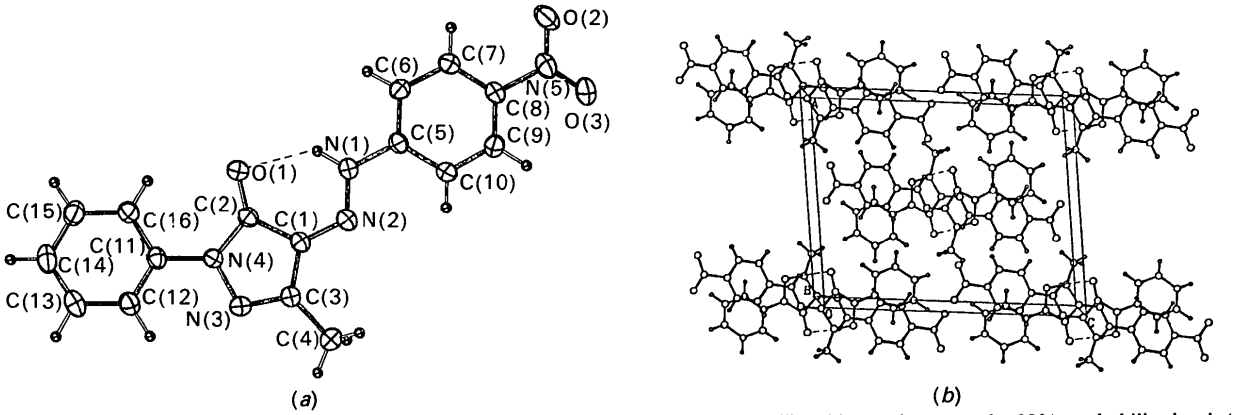
Class 1 **Class 2** **Class 3**

θ_1 = O=C—C; θ_2 = C—C=N; θ_3 = C=N—N

Compound or Refcode	d(N···O) (Å)	Λ	θ_1 (°)	θ_2 (°)	θ_3 (°)	δ(NH) (p.p.m.)	ν(NH) (cm^{-1})	Ref.
Class 1: Ketohydrazones with fused isoxazole ring								
(1)	2.925 (2)	0.49	131.3 (2)	129.7 (1)	119.2 (1)	12.70	3209	p.w.
(2)	2.882 (2)	0.56	129.8 (2)	129.5 (2)	119.2 (2)	12.65	3212	p.w.
(3*A*)	2.853 (6)	0.51	133.4 (5)	128.1 (5)	116.8 (4)	12.57	3216	p.w.
(3*B*)	2.887 (6)	0.52	128.7 (5)	129.6 (5)	119.9 (4)	12.57	3216	p.w.
⟨Average⟩	2.89 [3]	0.52 [2]	131 [2]	129.2 [6]	119 [1]	12.64 [5]	3212 [3]	
Class 2: Ketohydrazones with fused pyrazole ring								
(4)	2.783 (3)	0.56	127.4 (2)	128.7 (2)	117.5 (2)	13.60	3100	p.w.
JEBMEI	2.714 (4)	0.52	127.5 (4)	127.3 (3)	115.9 (3)	–	–	(*a*)
VUXVAL	2.746 (3)	0.55	127.4 (2)	128.0 (2)	116.3 (2)	–	–	(*b*)
VUYHEC	2.755 (2)	0.62	127.1 (2)	128.4 (2)	116.5 (2)	–	–	(*c*)
DODDAB01	2.807 (8)	0.50	128.1 (3)	128.2 (3)	118.4 (3)	–	–	(*d*)
DODDAB02	2.755 (8)	0.48	128.8 (7)	127.2 (6)	116.9 (5)	–	–	(*e*)
⟨Average⟩	2.76 [3]	0.54 [5]	127.7 [6]	128.0 [5]	116.9 [8]			
Class 3: Diketohydrazones (average on 11 molecules)								
⟨Average⟩	2.58 [2]	0.45 [7]	119.3 [6]	122 [6]	121.2 [8]	14.2 [6]	3081 [52]	(*f*, *g*)

p.w. = present work. (*a*) Connor, Kennedy, Dawes, Hursthouse & Walker (1990); (*b*) Whitaker (1988*a*); (*c*) Whitaker (1988*b*); (*d*) Whitaker (1991); (*e*) Whitaker (1992); (*f*) Bertolasi *et al.* (1993); (*g*) Bertolasi *et al.* (1994).

crystal by means of π–π interactions (Hunter & Sanders, 1990), as illustrated in the example of Fig. 5. In (1), (2) and (4), molecules are stacked in a centrosymmetric arrangement with consequent antiparallel orientations of the molecular dipoles; in (3) they are faced parallel to each other and reciprocally shifted, probably to avoid the repulsions between atoms carrying charges of the same sign. For all compounds the shortest interactions are of the order 3.3–3.4 Å (Table 6), which are typical of this kind of packing. The asymmetric unit of compound (3) consists of two independent molecules, *A* and *B*. Their packing consists of distinct stacks of molecules of types *A* or *B* linked by means of lateral bifurcated intermolecular N—H···O bonds and short C—H···O contacts. Molecules *A* and *B* display different N···O hydrogen bond lengths [2.853 (6) and 2.887 (6) Å] and other unusual differences in bond distances and



(*a*) (*b*)

Fig. 4. (*a*) *ORTEP* (Johnson, 1976) view and atom numbering for (4). The thermal ellipsoids are drawn at the 30% probability level. (*b*) Unit cell and its contents.

Table 6. *Lengths of specific stacking contacts less than 3.40 Å*

(1)	
N(2)···C(5')	3.398 (2)
C(2)···C(9')	3.381 (2)
C(3)···C(7'')	3.368 (2)
(2)	
O(1)···N(4''')	3.373 (2)
N(2)···C(7''')	3.400 (2)
C(5)···C(5''')	3.312 (2)
O(3)···N(2'')	3.351 (2)
O(3)···C(1'')	3.289 (3)
N(2)···N(4'')	3.251 (2)
C(5)···C(9'')	3.348 (3)
(3)	
N(2*A*)···C(8*A*')	3.302 (7)
C(2*A*)···C(6*A*')	3.383 (7)
C(3*A*)···C(10*A*')	3.393 (7)
N(2*B*)···C(8*B*''')	3.312 (6)
C(2*B*)···C(6*B*''')	3.295 (7)
C(3*B*)···C(10*B*)	3.383 (7)
(4)	
O(1)···C(3''')	3.338 (3)
N(1)···N(4''')	3.355 (3)
C(1)···C(2''')	3.335 (3)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iii) $1-x, -1-y, -z$; (iv) $2-x, -1-y, -z$; (v) $x, y+1, z$; (vi) $x, y-1, z$; (vii) $2-x, 1-y, -z$.

angles (Table 3). The greatest differences concern the ketohydrazone moiety; for instance, the C(5)—N(1)—N(2) angle is 117.4 (4) in *A* and 123.7 (4)° in *B* and the C(1)—C(2)—O(1) angle is 133.4 (5)° in *A* and 128.7 (5)° in *B*, while the C(1)—C(2) distance is 1.421 (7) in *A* and 1.468 (7) Å in *B*. Such large discrepancies are difficult to be explained. Apparently, the combination of the abnormal flexibility of the ketohydrazone group combined with the coupling of hydrogen-bond strengthening and π-delocalization typical of RAHB make the molecule, in some way, more plastic than elastic, and, therefore, more inclined to change its shape in such a way to achieve the most efficient $\pi-\pi$ packing.

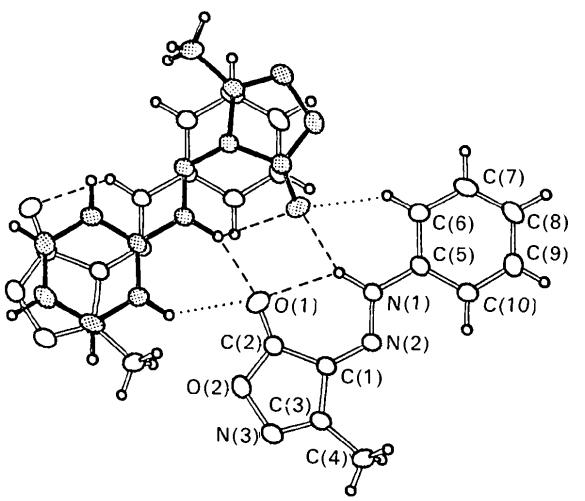


Fig. 5. View of the simultaneous formation of $\pi-\pi$ stacking interactions, N—H···O hydrogen bonds (broken lines) and C—H···O short contacts (dotted lines) in the crystal packing of (1).

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SHORT COMMUNICATIONS

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The structures of dimethylammonium metal(III) sulfate hexahydrates (metal = Al, Cr).

BY VLADIMIR M. PETRUŠEVSKI, *Institute of Chemistry, Faculty of Natural Sciences and Mathematics, POB* 162, 91001 *Skopje, Macedonia*

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Abstract

In a recent article [Galešić & Jordanovska (1992). *Acta Cryst.* C**48**, 256–258], the structures of $[Al(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$ and the corresponding chromium analogue were refined in the $P2_1n$ space group. Despite the formal difference between the formula unit of these compounds, $RM^{III}(SO_4)_2.6H_2O$, and the general formula of the Tutton salts, $M^I_2M^{II}(SO_4)_2.6H_2O$, both studied compounds may be considered as variations in the Tutton salt structure.

Alums and Tutton salts are two very large classes of double salts. The general formula of the alums is $M^IM^{III}(XY_4).12H_2O$ and that of Tutton salts is $M^I_2M^{II}(XY_4)_2.6H_2O$. In both classes of compounds, $M^I = K^+$, Rb^+, Cs^+, Tl^+, NH_4^+ and $XY_4 = SO_4^{2-}$, SeO_4^{2-}, BeF_4^{2-}. However, for the alum family, M^I might also be $CH_3NH_3^+$, NH_3OH^+, $N_2H_5^+$, $C(NH_2)_3^+$ *etc.* On the other hand, CrO_4^{2-} Tutton salts have been proven to exist. The nature of M^{II} is specific for Tutton salts only ($M^{II} = Mg^{2+}$, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ru^{2+}) and M^{III} is specific for alums ($M^{III} = Al^{3+}$, Ga^{3+}, In^{3+}, Sc^{3+}, Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Mo^{3+}, Ru^{3+}, Rh^{3+}, Ir^{3+}).

As long as the formula is considered, the title compounds resemble the alum family, with the exception that they are hexahydrates rather than dodecahydrates. Probably for this reason the authors (Galešić & Jordanovska, 1992) discussed the crystal structures of $[Al(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$ and $[Cr(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$ in relation to the alum structures: the mean Al—O*w* distance was basically the same as in a number of alum structures and the $(CH_3)_2NH^+$ group was disordered around the inversion center – as are NH_4^+, NH_3OH^+ and $CH_3NH_3^+$ – in the corresponding Al alums *etc.* (Lipson, 1935; Fletcher & Steeple, 1964; Abdeen, Will & Weiss, 1981; Abdeen *et al.*, 1981). However, both compounds crystallize in the space group $P2_1/c$, thus making impossible any further comparison with the cubic ($Pa3$) alums.

It is interesting to note that the similarities between the diethylammonium aluminium sulfate hexahydrate (DAlSH) and diethylammonium chromium sulfate hexahydrate (DCrSH), on one hand, and the Tutton salts, on the other, are so close that not only are all these compounds isostructural, but the title compounds may even be encountered as a peculiar type of variation in this family of compounds. The following arguments may be given to support this assertion:

(*a*) The space group symmetry of the Tutton salts ($P2_1/a$) and of the title compounds ($P2_1/n$) is the same, as is the number of formula units (two) in the unit cell.

(*b*) The following structural characteristics are typical for the Tutton salts: six water molecules (three different types) at general positions, coordinated to a divalent metal which is on an inversion center; one type of tetrahedral anion and one type of univalent cation, all of which are at general positions. In the title compounds, six water molecules of three different types are found at positions of symmetry 1 and are coordinated to a *trivalent* (Al or Cr) metal cation, which is on an inversion center. Also, there is one type of tetrahedral anion at general positions and one type of univalent (dimethylammonium) cation disordered across an inversion center, with an occupancy factor of 0.5.* This disorder resembles that found in the alum family of crystals.

(*c*) The distortion indices (Baur, 1974) of the $AlOw_6$ ($CrOw_6$) octahedra are closer to the values found (Petruševski, 1990) in the Tutton salts than to those found in alums (*cf.* Table 1). Also, the SO_4 tetrahedra seem to have 'normal' bond lengths, as in the majority of the Tutton salts; in the alum family, as a result of extensive thermal motion, the S—O bond lengths are often slightly contracted (by as much as 0.02 Å) when compared (*cf.* Table 2) with the 'ideal' SO_4 bond length (Murray-Rust, Bürgi & Dunitz, 1978).† No disorder was found in the sulfate group (the sulfate groups in the α alums are, as a

* The authors (Galešić & Jordanovska, 1992) mention that the occupancy factors for Al, Cr and N are all 0.5, which is incorrect because Al (Cr) ions *fully occupy* the $\bar{1}$ positions. It is the *multiplicity* of these positions (2) that is one half of the multiplicity of the positions of general symmetry (4).

† The values for the S—O bond lengths in alums increase at low temperatures, as the thermal motion becomes less pronounced (Brorson & Gajhede, 1987; Best & Forsyth, 1991).