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Interactions of Aromatic Carboxylic Acids with Quinolin-8-ol (Oxine): Synthesis and the Crystal Structures of the Proton-Transfer Compounds with the Nitro-Substituted Benzoic Acids

Graham Smith,[A,B] *Urs D. Wermuth*[A] *and Jonathan M. White*[C]

[A] Centre for Instrumental and Developmental Chemistry, School of Physical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Qld. 4001.
[B] Author to whom correspondence should be addressed(e-mail: g.smith@qut.edu.au).
[C] School of Chemistry, University of Melbourne, Parkville, Vic. 3052.

Proton-transfer compounds of quinolin-8-ol (oxine) with the nitro-substituted aromatic carboxylic acids 2-nitrobenzoic acid, $[(C_9H_8NO^+)(C_7H_4NO_4^-)\cdot H_2O]$ (1), 3-nitrobenzoic acid, $[(C_9H_8NO^+)(C_7H_4NO_4)^-]$ (2), 4-nitrobenzoic acid, $[(C_9H_8NO^+)(C_7H_4NO_4^-)(C_7H_5NO_4)]$ (3), 3,5-dinitrobenzoic acid, $[(C_9H_8NO^+)_2(C_7H_3N_2O_6^-)_2\cdot 3H_2O]$ (4), 5-nitrosalicylic acid, $[(C_9H_8NO^+)\ (C_7H_4NO_5^-)]$ (5) and 3,5-dinitrosalicylic acid, $[(C_9H_8NO^+)(C_7H_3N_2O_7^-)]$ (6) have been prepared and characterized by using both infrared spectroscopy and single-crystal X-ray diffraction methods [(3), (4) and (6)]. In all compounds, protonation of the quinoline nitrogen occurs together with primary hydrogen-bonding interactions involving this group and the carboxylate group of the acid, while further peripheral associations, in the case of the trihydrate (4), also involving the water molecules, result predominantly in simple chain polymeric structures.

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Introduction

Quinolin-8-ol [8-hydroxyquinoline (oxine)] is well known as a disinfectant and antiseptic agent as well as being a particularly versatile molecule for use in metal complex chemistry. The relative positions of the hetero-nitrogen (pK_a 10.8) and 8-substituted phenol group, together with the acidic nature of the latter (pK_a 4.9), provide the textbook example for selective interaction with metals, giving bis- and tris-chelate complex systems which are often neutral. Under basic conditions, essentially no selectivity is achieved but with pH control, quantitative precipitation is possible, such as with Mg^{2+} where the complex $[Mg(oxine^-)_2]$ is a common weighing form in gravimetric analysis.[1] While neutral divalent metal complexes such as this and $[Pd(oxine^-)_2]$[2] are common, adducts involving metal complexes or metal salts with free oxine are also known, e.g. $\{[Ni(oxine^-)_2]\cdot oxine\}$,[3] $[K^+(oxine^-)\cdot oxine]$[4] and $[K^+(oxine^-)\cdot(oxine)_2]$.[5] In addition, metal complexes with both anionic and neutral coordinated oxine species have been reported, e.g. $\{[Ag(oxine^-)(oxine)]\cdot pyridine\}$[6] and the Ag complex unit in $\{[Ag(oxine)_2]^+(p\text{-toluenesulfonate}^-)\}$.[7]

Neutral adducts with organic compounds are less prevalent, but the structures of stable 1:1 adducts with chloranil[8] and 1,3,5-trinitrobenzene[9] are known together with the 2:1 proton-transfer adduct with 1,2,3-trihydroxybenzene, $[(oxine^+)(thb^-)\cdot oxine]$.[10] In the neutral adducts, the oxine forms cyclic $R_2^2(8)$ hydrogen-bonded dimers via the hetero-nitrogen and the phenolic oxygen, with peripheral secondary hydrogen bonds giving polymer structures. This basic dimer is similar to what is found in the crystal structure of the parent oxine.[11]

Previous preliminary work by our group on cocrystals of aromatic carboxylic acids with oxine gave some crystals which proved unsuitable for structural analysis by single-crystal X-ray methods[12] because of an apparent tendency for twinning, while in its adduct with Kemp's triacid (*cis*,*cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid), $[(oxine^+)_2(C_{12}H_{17}O_6^-)_2\cdot n(oxine)]$,[13] the partial disordered oxine molecule in the lattice was progressively lost during data collection without apparent destruction of the crystallinity of the compound. This matter has been further addressed in this study because of a similar occurrence with one of the reported compounds. Reported here is the preparation and characterization using spectroscopic and single-crystal X-ray diffraction of a series of six proton-transfer compounds of quinolin-8-ol (oxine) with the nitro-substituted aromatic carboxylic acids 2-nitrobenzoic acid (2-nba), $[(oxine^+)(2\text{-}nba^-)\cdot H_2O]$ (1), 3-nitrobenzoic acid (3-nba), $[(oxine^+)(3\text{-}nba^-)]$ (2), 4-nitrobenzoic acid (4-nba), $[(oxine^+)(4\text{-}nba^-)(4\text{-}nba)]$ (3), 3,5-dinitrobenzoic acid (dnba), $[(oxine^+)_2(dnba^-)_2\cdot 3H_2O]$ (4), 5-nitrosalicylic acid (5-nsa), $[(oxine^+)(5\text{-}nsa^-)]$ (5), and 3,5-

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dinitrosalicylic acid (dnsa), [(oxine$^+$)(dnsa$^-$)] (6). The crystal structures of three of these [(3), (4) and (6)] have been determined by single-crystal X-ray diffraction methods.

Results

Final atomic coordinates, bond distances and angles, anisotropic thermal parameters and hydrogen atom coordinates for adducts (3), (4) and (6) have been deposited as an Accessory Publication.* Atom numbering schemes for the associated molecule types and the hydrogen-bonding schemes are shown in Figs 1–4.

Discussion

In all compounds reported here, as predicted on the basis of pK_a differences, proton transfer from the carboxylic acid group to the hetero-nitrogen of the oxine molecule occurs, together with primary O···N hydrogen-bond formation between donor and acceptor atoms. However, in none of the compounds do we find a primary cyclic hydrogen-bonded $R_2^2(8)$ A–B heterodimer formed, involving the second carboxylate oxygen and the 8-hydroxy substituent of oxine; nor are there any A–A or B–B homodimers found (as with the parent acids or with oxine itself [11]). Instead, this molecule acts in a bridging mode to link the associated molecular units into chain polymers through hydrogen bonds. In addition, this adduct series with oxine shows a greater tendency for formation of various stoichiometric ratios than any of the previously studied Lewis base types.

[(oxine$^+$)(4-nba$^-$)(4-nba)] (3)

The structure of the 1 : 2 adduct of quinolin-8-ol with 4-nitrobenzoic acid [(oxine$^+$)(4-nba$^-$)(4-nba)] (3) (Fig. 1) comprises an A–A–B repeating unit in which the primary interaction, after proton transfer from the first carboxylic acid to the hetero-nitrogen of oxine, is formation of a single hydrogen bond [N(1)–H(1)···O(7), 2.730(3) Å; N–H···O, 147(3)°]. The second carboxyl oxygen then forms a single hydrogen bond with the carboxyl group of the second (protonated) 4-nba molecule [O(6)···H(1)–O(2), 2.572(3) Å; O···H–O, 170(3)°]. The polymer link is provided by the oxine molecule through the 8-hydroxy group to a carboxylate oxygen of the first 4-nba molecule [O(1)–H(24)···O(6)^a, 2.730(3) Å; O–H···O, 147(3)° (a = 1+x, y, z)], giving a three-centre interaction about O(6). The resulting chains form along the a cell direction (Fig. 2). Neither the second

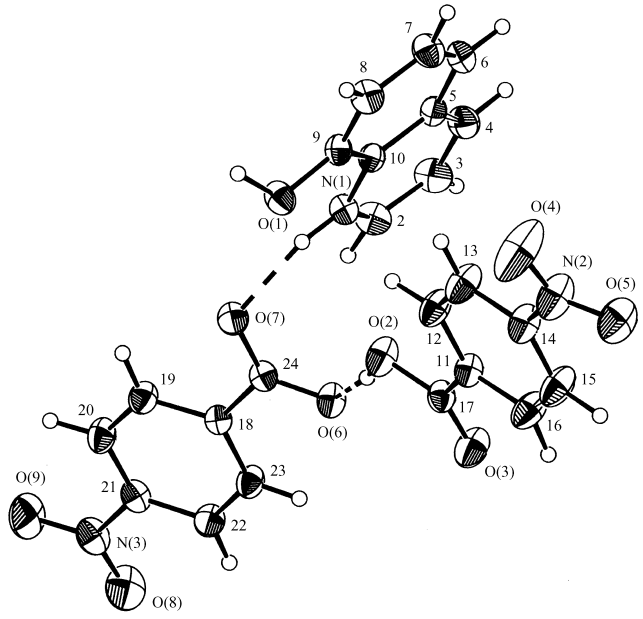

Fig. 1. Molecular configuration and atom numbering for the three molecules in the hydrogen-bonded A–A–B trimer in adduct (3). Unless otherwise indicated, atoms are carbon.

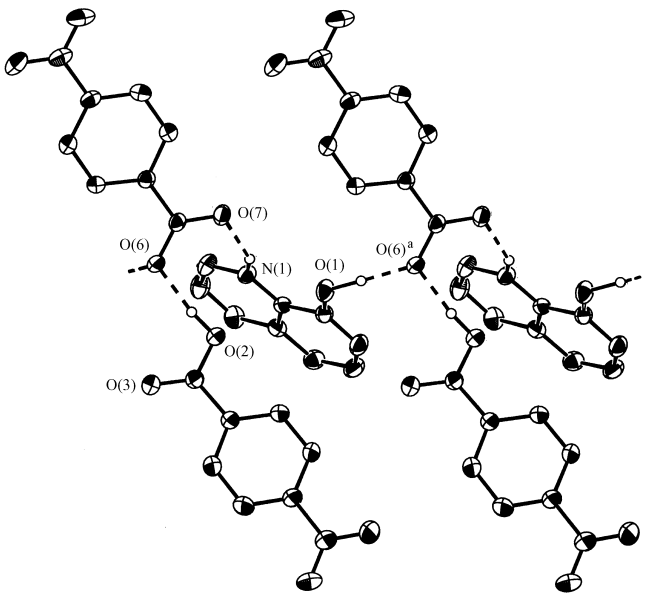

Fig. 2. Extension of the trimer units in (3) through peripheral hydrogen bonds in the a cell direction.

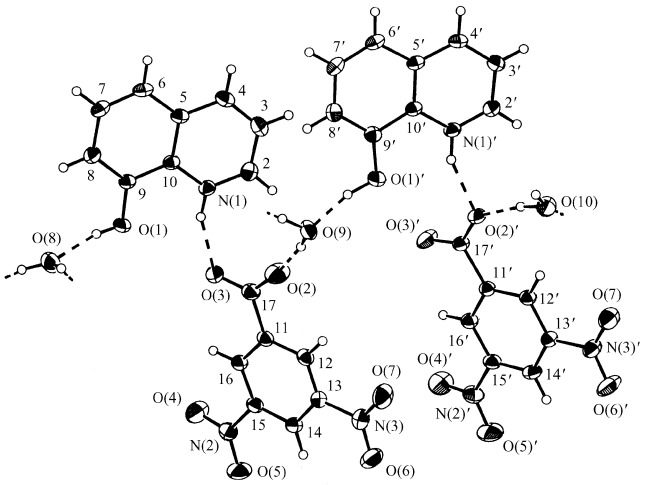

Fig. 3. Atom numbering scheme and hydrogen bonding (shown as broken lines) in the adduct hydrate (4).

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carboxyl oxygen of molecule 2 nor the nitro groups of either acid are involved in hydrogen bonding.

[(oxine$^+$)$_2$(dnba$^-$)$_2$·3H$_2$O] (4)

In the 2 : 2 adduct trihydrate of oxine with 3,5-dinitrobenzoic acid, [(oxine$^+$)$_2$(dnba$^-$)$_2$·3H$_2$O] (4), the primary A–B interaction similar to that found in adduct (3) is present in both independent molecule pairs in the asymmetric unit [N(1)–H(11)···O(3), 2.829(3) Å; N–H···O, 156(3)°; N(1′)–H(11′)···O(2′), 2.701(3) Å; N–H···O, 152(3)°]. The A–B pairs are joined into a ribbon polymer (Fig. 3) by peripheral hydrogen bonds to the three water molecules [O(8), O(9), O(10)] linking the carboxyl oxygens and the 8-hydroxy substituent of the oxine molecules [O(2)···H(9A)–O(9), 2.686(3) Å; O···H–O, 169(3)°; O(9)···H(1′)–O(1′), 2.545(3) Å; O···H–O, 165(3)°; O(9)–H(9B)···O(3′)[a], 2.690(3) Å; O–H···O, 175(3)° (a = 1 – *x*, ½+*y*, 1 – *z*); O(2′)···H(10B)–O(10), 2.754(3) Å; O–H···O, 169(3)°; O(8)···H(1)–O(1), 2.671(3) Å; O···H–O, 167(3)°; O(8)–H(8B)···O(3)[b], 2.707(3) Å; O–H···O, 171(3)° (b = –*x*, ½+*y*, 1 – *z*)]. The water molecules also mutually interact [O(8)–H(8A)···O(10)[a], 2.772(3) Å; O–H···O, 175(3)°; O(10)–H(10A)···O(8)[c], 2.958(3) Å; O–H···O, 158(3)° (c = 1+*x*, *y*, *z*)].

No nitro-group participation in hydrogen bonding is found.

[(oxine$^+$)(dnsa$^-$)] (6)

The 1 : 1 proton-transfer compound of oxine with 3,5-dinitrosalicylic acid, [(oxine$^+$)(dnsa$^-$)], is similar to the previously discussed carboxylic acid–oxine cocrystals in having the primary hydrogen-bonded dimeric repeat within all four hetero-pairs in the crystallographic repeating unit (Fig. 4). All interactions between the quinolinium proton and the carboxylate oxygen are dimensionally and geometrically similar [N(1)–H(1)···O(4), 2.730–2.790(9) Å; N–H···O, 149–160(4)°]. Similar extensions to those found in (4) and (5) via strong peripheral hydrogen bonds linking the protons of the 8-hydroxy substituent of oxine with one of the carboxyl oxygens of dnsa are also found [O(1)–H(1)···O(3′′)[a], 2.567(9) Å; O–H···O, 173(3)° (a = 1+*x*, *y*, *z*); O(1′′)–H(1′′)···O(3)[b], 2.562(9) Å; O–H···O, 171(3)° (b = –1+*x*, –1+*y*, *z*); O(1:)–H(1:)···O(3′)[c], 2.591(9) Å; O–H···O, 168(3)° (c = –2+*x*, –1+*y*, *z*); O(1′)–H(1′)···O(3)[d], 2.561(9) Å; O–H···O, 165(3)° (d = *x*, *y*, *z*)]. The result is a hydrogen-bonded chain polymer structure. Unlike a number of the compounds involving the nitrosalicylic acids,[14,15] no interactions involving the nitro oxygens are present. However, this structure shows significant π–π association between the dnsa and oxine molecules, a feature not common among either the neutral or proton-transfer compounds or adducts of the nitro-substituted aromatic carboxylic acids. Also as expected, and similar to the parent acid and its compounds, the intramolecular O(hydroxyl)···O(carboxyl) hydrogen bond is present [O(2)···O(4), 2.462–2.472(8) Å].

Some disorder and minor conformational variation in the nitro groups of the dnsa molecules are present but are not sufficient to contribute to the more serious structural problem (described in Experimental), which manifests itself as pseudo-symmetry (both translation and inversion) among the four sets of molecular pairs in the crystallographic asymmetric unit. By a legal shift of the origin in the space group *Pc* in both the *x* direction (0.390) and the *y* direction (0.063), a pseudo-translation (*x*, ½+*y*, *z*) is created, relating the X, X′′ and X:, X′ pairs. In addition, a pseudo-inversion centre at ($^1/_2$, $^5/_8$, $^1/_2$) would create the $P2_1/c$ cell (with the *b* axis halved) from the previous unsuccessful structure determination attempt.[12] Such pseudo-symmetry identifies the possible presence of a stacking fault or inversion-related twinning. The presence of the 'ghost' oxine may be an artefact of such phenomena if ignored[16] but the computational treatment necessary to handle the problem will not be considered here. This argument, however, would tend to obviate oxine as a contributing factor, having, as previously mentioned, a tendency to act as a labile molecule of crystallization despite its moderate melting temperature (76°C). This was definitely the case with the cyclic 2 : 2 proton-transfer compound with Kemp's triacid where a labile disordered partial unassociated oxine molecule (occupancy ca. 0.9) existed beside the stable dimeric acid–oxine cage structure.[13] Oxine has been observed to undergo intrusive solid-state reaction by diffusion into certain anhydrides,[17] nitrophenols,[18] salicylic acid[19] and metal salts.[20] The formation of the 2 : 1 proton-transfer adduct with 1,2,3-trihydroxybenzene also proceeds in a similar manner by intrusive solid-state reaction.[10] Of possible relevance to the present examples, it was observed that with the nitrophenols,[18] reaction proceeded more readily with increased nitro-group substitution and with increased molecular symmetry. It must be generally assumed that both types of solid-state reaction involving oxine (either intrusive or effusive, usually without crystal breakdown), occur by similar mechanisms.

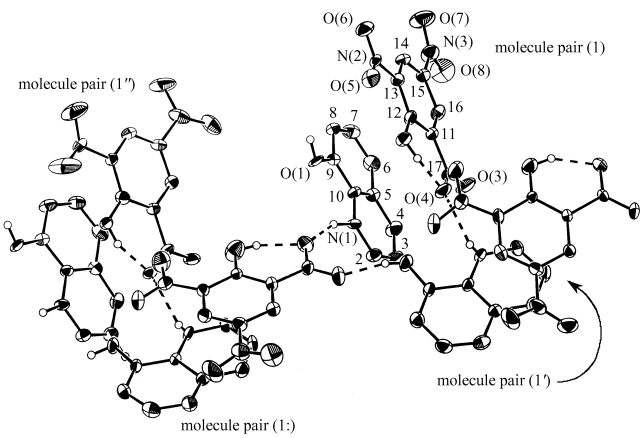

Fig. 4. Atom numbering scheme and hydrogen bonding involving the four independent A–B dimers in the crystallographic repeating unit in the adduct (6).

Experimental

All complexes were prepared from 1 : 1 molar amounts of quinolin-8-ol (0.2 g, 1.4 mmol) and respectively, 2-nitrobenzoic acid (1), 3-nitrobenzoic acid (2), 4-nitrobenzoic acid (3), 3,5-dinitrobenzoic acid

(4), 5-nitrosalicylic acid (5) and 3,5-dinitrosalicylic acid (6). Preparations involved heating under reflux for 10 min at ca. 90°C in 20 cm^3 of 95% ethanol, the product being subsequently obtained by the partial or total evaporation of the solvent at room temperature, yielding for (1) large yellow *prisms* (m.p. 88–90°C); for (2), yellow *microcrystals* (m.p. 130–131°C); for (3), yellow *prisms* (m.p. 195–198°C); for (4), yellow *prisms* (m.p. 161–162.5°C); for (5) a yellow *powder* (m.p. 180–182°C); for (6) orange *needles* (m.p. 244–250°C). Elemental analyses indicated 1 : 1 stoichiometries for all adducts except (3) (1 : 2), while (1) was a monohydrate. With (4), the presence of 1.5 waters was found from analysis, later confirmed in the crystal structure determination as a 2 : 2 trihydrate. Found for (1): C, 58.2; H, 4.3; N, 8.5. $C_{16}H_{14}N_2O_6$ requires C, 58.2; H, 4.2; N, 8.5%. Found for (2): C, 61.5; H, 3.8; N, 8.8. $C_{16}H_{12}N_2O_5$ requires C, 61.5; H, 3.8; N, 9.0%. Found for (3): C, 57.7; H, 3.6; N, 8.8. $C_{23}H_{17}N_3O_9$ requires C, 57.6; H, 3.6; N, 8.8%. Found for (4): C, 50.0; H, 3.5; N, 10.8. $C_{32}H_{28}N_6O_{17}$ requires C, 50.0; H, 3.7; N, 10.9%. Found for (5): C, 58.5; H, 3.6; N, 8.3. $C_{16}H_{12}N_2O_6$ requires C, 58.5; H, 3.7; N, 8.5%. Found for (6): C, 51.8; H, 2.9; N, 11.3. $C_{16}H_{11}N_3O_8$ requires C, 51.5; H, 3.0; N, 11.3%.

Attempts to prepare the adduct with 1,3,5-trinitrobenzoic acid using either the general refluxing method in ethanol at elevated temperature or the room-temperature variant (because of the ease of decarboxylation of the acid even at moderate temperature) gave good crystals of the previously described 1 : 1 oxine–1,3,5-trinitrobenzene adduct.[9] Infrared spectra were recorded for all samples as pressed disks in KBr on a Perkin–Elmer Spectrum 1000 Fourier-transform infrared spectrometer.

Crystallography

Crystal Data

(3) $[(C_9H_8NO^+)(C_7H_4NO_4^-)(C_7H_5NO_4)]$, CCDC 164598, mol. wt 479.4, triclinic, space group $P\bar{1}$, a 7.052(2), b 7.497(2), c 21.121(6) Å, α 97.94(2), β 97.35(3), γ 99.45(2)°, V 1077.9(5) $Å^3$, F(000) 496, Z 2, D_c 1.477 g cm^{-3}, μ(Mo Kα) 1.16 cm^{-1}, temperature 293(2) K. 4089 reflections measured [$2\theta_{max}$ 51°: h, 0 to 8; k, –8 to 8; l, –25 to 24], 3756 unique (R_{int} 0.012). Final R_1* 0.048 (F); wR_2† 0.123 (F^2) [2845 observed with $I > 2.0\sigma(I)$]; S 1.03. Crystal size 0.50 by 0.30 by 0.25 mm; max/min transmission factors, 0.82/0.70.

(4) $[(C_9H_8NO^+)_2(C_7H_3N_2O_6^-)_2{\cdot}3H_2O]$, CCDC 164597, mol. wt 768.6, monoclinic, space group $P2_1$, a 14.9606(6), b 7.4287(5), c 15.633(1) Å, β 102.170(4)°, V 1698.4(2) $Å^3$, F(000) 796, Z 2, D_c 1.503 g cm^{-3}, μ(Cu Kα) 1.22 cm^{-1}, temperature 293(2) K. 3851 reflections measured [$2\theta_{max}$ 150°: h, –18 to 0; k, 0 to 9; l, –19 to 19], 3705 unique (R_{int} 0.022). Final R_1 0.029 (F); wR_2 0.084 (F^2) [3564 observed with $I > 2.0\sigma(I)$]; S 1.04; absolute structure parameter, 0.01(15). Crystal size 0.43 by 0.30 by 0.23 mm.

(6) $[(C_9H_8NO^+)(C_7H_3N_2O_7^-)]$, CCDC 164599, mol. wt 373.3, monoclinic, space group Pc, a 8.015(2), b 15.010(2), c 26.546(2) Å, β 95.52(2)°, V 3178.8(9) $Å^3$, F(000) 1536, Z 8, D_c 1.560 g cm^{-3}, μ(Cu Kα) 1.11 cm^{-1}, temperature 293(2) K. 7322 reflections measured [$2\theta_{max}$ 140°: h, –6 to 9; k, –12 to 18; l, –32 to 32], 7103 unique (R_{int} 0.013). Final R_1 0.080 (F); wR_2 0.210 (F^2) [6101 observed with $I > 2.0\sigma(I)$]; S 1.03; absolute structure parameter, 0.4(3). Crystal size 0.78 by 0.21 by 0.14 mm; max/min transmission factors, 0.87/0.64.

Data Collection, *Structure Solution and Refinement*

X-Ray diffraction data for all compounds were measured on Enraf–Nonius CAD-4 diffractometers by using either crystal-monochromatized Mo Kα X-radiation (λ 0.71073 Å) [compound (3)] or Cu Kα X-radiation (λ 1.5418 Å) [compounds (4) and (6)]. Negligible change in the intensities of three standards monitored throughout the data collection periods for all adducts indicated no significant crystal decomposition. Data were corrected for Lorentz and polarization effects, extinction and for absorption [(3) and (6) only (analytical, Gaussian)]. The structures were solved by direct methods and refined by full-matrix least-squares (on F^2) by using SHELXL-97[21] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms involved in the hydrogen-bonding interactions were located by difference methods and both positional and thermal parameters were refined while others were generally included at calculated positions in the refinements as riding models. The values of A and B in the weighting scheme $w = [\sigma^2(F_o)^2+(AP)^2+BP]^{-1}$ {where P = [max. $(F_o^2,0)+2(F_c)^2]/3$} were 0.0783, 0.2461 (3), 0.0593, 0.1264 (4), and 0.1826, 0.7519 (6). With (3), the high thermal motion of the nitro-oxygens of molecule 1 [O(4) and O(5)] resulted in these being modelled over two independent sites with occupancies of 0.80 and 0.20 respectively. Compound (6), which we had previously investigated unsuccessfully crystallographically,[12] when it was found to have what appeared to be bad disorder in the space group $P2_1/c$ with Z 4 in a unit cell with half the present b axial parameter, was resolved in the lower-symmetry space group Pc with Z 8. In this space group, pseudo-symmetry is present with the molecules related by an approximate 2_1 screw operation and inversion symmetry. This is somewhat analagous to, but not as severe as, the modulated structure described for the 1 : 1 proton-transfer adduct of 2,4,6-trinitrobenzoic acid with 2,6-diaminopyridine.[22] In addition, the presence of a partial disordered labile molecule of oxine contributes to the high refinement residual which could be reduced from the table value (R 0.080) to ca. R 0.05 by incorporating electron density equivalent to 90% of a ghost oxine molecule having an occupancy of 0.08. This effect may also be due to the presence of an overriding but inadequately modelled stacking fault or an inversion twin. However, this structural problem could not be further handled in this study and furthermore, the Pc model adequately describes the basic hydrogen-bonded structural framework which is not altered by the presence of the the unasssociated 'ghost oxine'. A similar phenomenon was observed for the structure of the 1 : 1 proton-transfer compound of Kemp's triacid with oxine,[13] in which a partial disordered oxine molecule of crystallization was lost progressively with time during room-temperature data collection, without significant loss in crystallinity.

Conclusions

The series of quinolin-8-ol compounds with the nitro-substituted benzoic acids studied here shows a greater variability in composition and form than any of the other Lewis-base compounds of the same acids previously studied. The incorporation of water into the cocrystal make-up in two of the examples [(1) and (4)] obviously influences the stabilization of the crystal lattice, which in the case of the trihydrate (4) links together rows of oxine and dnba molecules to give an very stable and ordered structure. This is in contrast to the 1 : 1 compound with dnsa (6), where a probable stacking fault is present in the structure, and may be similar to the badly twinned monohydrate (1) where no structural analysis was possible, despite its macro-crystalline morphology. Infrared spectroscopy has also proved useful, as previously noted,[23] for the recognition of proton transfer in compounds of the type found in this series, particularly with those for which crystal structure determinations are not possible e.g. (1), (2) and (5). As with the parallel study involving the same series of acids with the analogous nitrogen base 8-aminoquinoline,[24] disappearance of the characteristic strong C=O stretching frequency at ca.1700 cm^{-1} is the most definitive sign in the composite spectrum of proton transfer [except in the case of the 1 : 2 adduct (3) where free acid is present]. The accompanying broad $=N-H^+$

*$R_1 = (\Sigma\,|F_o|-|F_c|)/(\Sigma\,|F_o|)$.
†$wR_2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, w(F_o^2)^2]^{½}$.

absorptions expected in the 2700–2250 cm^{-1} region of the spectrum[25] are invariably unresolved within the broad and extended hydrogen-bonded –OH absorptions centred typically at ca. 3400 cm^{-1} [range: 3391 (2) to 3446 cm^{-1} (6)], similar to those in the parent oxine (3405 cm^{-1}).[26] However, infrared spectroscopy remains a useful tool for the identification of the nature of the interaction in such compounds.

Acknowledgments

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