Hydrogen Bonding and Polymorphism of Amino Alcohol Salts with Quinaldinate: Structural Study

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Abstract: Three amino alcohols, 3-amino-1-propanol (abbreviated as 3a1pOH), 2-amino-1-butanol (2a1bOH), and 2-amino-2-methyl-1-propanol (2a2m1pOH), were reacted with quinoline-2-carboxylic acid, known as quinaldinic acid. This combination yielded three salts, (3a1pOHH)quin (1, 3a1pOHH⁺ = protonated 3-amino-1-propanol, quin⁻ = anion of quinaldinic acid), (2a1bOHH)quin (2, 2a1bOHH⁺ = protonated 2-amino-1-butanol), and (2a2m1pOHH)quin (3, 2a2m1pOH⁺ = protonated 2-amino-2-methyl-1-propanol). The 2-amino-1-butanol and 2-amino-2-methyl-1-propanol systems produced two polymorphs each, labeled 2a/2b and 3a/3b, respectively. The compounds were characterized by X-ray structure analysis on single-crystal. The crystal structures of all consisted of protonated amino alcohols with NH₃⁺ moiety and quinaldinate anions with carboxylate moiety. The used amino alcohols contained one OH and one NH₂ functional group, both prone to participate in hydrogen bonding. Therefore, similar connectivity patterns were expected. This proved to be true to some extent as all structures contained the NH₃⁺···−OOC heterosynthon. Nevertheless, different hydrogen bonding and π···π stacking interactions were observed, leading to distinct connectivity motifs. The largest difference in hydrogen bonding occurred between polymorphs 3a and 3b, as they had only one heterosynton in common.

Keywords: hydrogen bond; synthon; crystal structure; polymorphism; amino alcohols; quinaldinic acid

1. Introduction

Crystal engineering, defined as preparation of new molecular solids with tailor-made properties by using intermolecular interactions [1], continues to draw the interest of a wide scientific community. A rational design of these solids is based on a thorough understanding of the supramolecular chemistry of functional groups, in particular those with a hydrogen bonding potential. Owing to their strength and directionality, hydrogen bonds are likely to dominate above all the other interactions. The extensive surveys of the Cambridge Structural Database (CSD) helped with the formulation of empirical guidelines concerning the design of molecular crystals [2]. A generally valid rule on hydrogen bonding states that all good proton donors and acceptors are normally engaged in interactions [3]. A new terminology has also emerged: a pair of complementary functional groups, linked via intermolecular interaction, such as a hydrogen bond, is known as a synthon [4]. A heterosynthon is composed of two different functional groups, whereas two identical groups make part of a homosynthon. A prominent example of a self-association motif is a well-known carboxylic acid dimer. Another rule concerns the synthon hierarchy: the heterosynthons are favored over the homosynthons. Recent reports agree that it is still impossible to predict the structure of the molecular solid [5,6]. In this context, a phenomenon of polymorphism is brought up. The term polymorphism describes the existence of the same compound in several crystal forms that differ in spatial arrangements of their components and some of their properties [7]. Polymorphs of the same compound
generally differ in lattice energies by a few kJ/mol at most [8]. As claimed by McCrone [9], the number of forms known for a given compound is proportional to the time and money spent in research on that compound. A systematic study of crystal structures of a large number of molecular solids, fueled also by the pharmaceutical industry [10,11], has revealed that at least every other molecule exhibits polymorphism [12]. It has been shown that hydrogen bonding potential only slightly increases a likelihood for the molecule to be polymorphic, whereas chiral molecules are somewhat reluctant towards crystallization in more than one crystal form [13].

Herein, the solid-state structures of salts of three amino alcohols with quinaldinic acid are presented. The structural formulae of the acid and amino alcohols are depicted in Figure 1.

Figure 1. Structural formulae of quinaldinic acid, 3-amino-1-propanol, 2-amino-1-butanol, and 2-amino-2-methyl-1-propanol.

The salts contained protonated amino alcohols as cations and quinaldinate ions as counter-ions. Single crystals of all were obtained inadvertently as by-products of the [Cu(quin)$_2$(H$_2$O)] reactions with the amino alcohol [14]. It has been observed previously that the amino alcohol OH group undergoes a spontaneous deprotonation in the presence of copper(II) complexes [15]. The resulting amino alcoholate ions coordinated to copper(II) in a chelating manner with the alkoxide oxygen serving as a bridge between two or among three metal ions. The amino alcoholate coordination probably assists in the deprotonation of amino alcohol. Some of our reaction systems provided a few more pieces of information concerning the formation of the amino alcoholate ions. The nature of the products, isolated from these reaction systems, strongly suggests a proton transfer from the OH group of the amino alcohol molecule to the NH$_2$ group of another molecule. In the reaction below, the H$_2$N–(CH$_2$)$_n$–OH denotes amino alcohol in general.

\[
2 \text{H}_2\text{N}-(\text{CH}_2)_n\text{OH} \leftrightarrow \text{H}_3\text{N}^+-(\text{CH}_2)_n\text{OH} + \text{H}_2\text{N}-(\text{CH}_2)_n\text{O}^-
\]

The H$_2$N–(CH$_2$)$_n$–O$^-$ ions coordinated to copper(II), whereas the H$_3$N$^+–(\text{CH}_2)_n$–OH ions crystallized as salts with quinaldinate. Later, a more straightforward synthesis of these salts was sought. A reaction of quinaldinic acid with the excess of amino alcohol in methanol with no copper(II) complex involved was met with success. Two of the salts were found to be polymorphic. A detailed account of the solid-state structures follows.

2. Results and Discussion

First, the common structural features of the title compounds are described. The crystal structures of all consist of NH$_2$-protonated amino alcohol molecules as counter-cations and quinaldinate anions with carboxylate moiety. In all, the C–O bond lengths of the carboxylate are the same within the experimental error. Interestingly, in some structures, the quinaldinate ions deviate from planarity. For convenience, we have described this deviation and the anions possess groups that are hydrogen bond donors (NH$_3^+$ in protonated amino
alcohol) or acceptors (carboxylate and quinaldinate nitrogen) or both (OH in protonated amino alcohol). With the first two being good hydrogen bond donors/acceptors, their participation in hydrogen bonding is likely to govern the connectivity patterns in solid state. A detailed list of hydrogen bonds is given in Table 2, whereas all possible heterosynthons and their actual occurrences in the structures of the title compounds are given in Table 3.

Table 1. \(\pi\cdots\pi\) stacking and C–H–\(\cdots\)π interactions [Å, °] in title compounds.

| Compound | Details |
|----------|---------|
| 1        | N\(\cdots\)O = 2.81(14) |
| 2a       | N\(\cdots\)O = 2.77(3) |
| 2b       | N\(\cdots\)O = 2.72(3) |
| 3a       | N\(\cdots\)O = 2.72(3) |
| 3b       | N\(\cdots\)O = 2.72(3) |

Table 2. Hydrogen bonds (Å) in title compounds.

| Compound | Synthon | Details |
|----------|---------|---------|
| 1        | NH\(_2^+\)…OOC | N\(\cdots\)O[2\(–\), 1\(–\), 2\(–\)] = 2.740(3) |
| 1        | NH\(_2^+\)…OOC | O\(\cdots\)O = 2.739(3) |
| 2a       | NH\(_2^+\)…OOC | N\(\cdots\)O[0.5+x, 0.5–y, 0.5+z] = 2.8216(16) |
| 2b       | NH\(_2^+\)…OOC | N\(\cdots\)O[1+x, y, z] = 2.948(2) |
| 3a       | NH\(_2^+\)…OOC | N\(\cdots\)N[1+x, y, z] = 3.080(3) |
| 3b       | NH\(_2^+\)…OOC | N\(\cdots\)N[1+x, y, z] = 3.080(3) |
Table 3. Heterosynthon occurrence in the structures of title compounds.

|                | 1    | 2a   | 2b   | 3a   | 3b   |
|----------------|------|------|------|------|------|
| \( \text{NH}_3^+ \cdots -\text{OOC} \) | ✓    | ✓    | ✓    | ✓    | ✓    |
| \( \text{OH} \cdots -\text{OOC} \)   | ✓    | ✓    | ✓    | ✓    | ✓    |
| \( \text{NH}_3^+ \cdots -\text{N(quin)} \) | ✓    | ✓    | ✓    | ✓    | ✓    |
| \( \text{NH}_3^+ \cdots -\text{OH} \)   | ✓    | ✓    | ✓    | ✓    | ✓    |

[a] Weak interaction. The N\( \cdots \)N contact is longer than the sum of the corresponding van der Waals radii, 3.1 Å [17].

The crystal structure of 1 consists of 3a1pOHH\(^+\) cations and strictly planar quinaldinate ions. All hydrogen bond donors and acceptors participate in intermolecular interactions. The quinaldinate nitrogen interacts only weakly with the NH\(^+\) group: the corresponding N\( \cdots \)N distance amounts to 3.108(3) Å, the value that is almost the same as the sum of the van der Waals radii for nitrogen atoms, 3.1 Å [17]. The connectivity pattern consists of two types of hydrogen bonds: the OH\( \cdots \)OOC and the NH\(^+\)\( \cdots \)OOC hydrogen bonds. Each type occurs between the cation and the anion. The hydrogen bonding pattern produces infinite layers, which are coplanar with the \( ab \) plane and stack along the \( c \) crystallographic axis. Section of such a layer is depicted in Figure 2. The layers stack upon one another with significant \( \pi \cdots \pi \) stacking interactions occurring between quinaldinates from adjacent layers (Figure S4). Parameters of the shortest \( \pi \cdots \pi \) stacking interaction are Ph\( \cdots \)Py type, \( C_g \cdots C_g = 3.6571(15) \) Å, dihedral angle = 0.41(11)°, shift distance = 1.346 Å.

![Figure 2](image-url)  
**Figure 2.** Perpendicular view to the section of a layer of hydrogen-bonded cations and anions in the structure of 1.

The 2-amino-1-butanol salt was found in two polymorphic forms, 2a and 2b. Both crystallize in a monoclinic \( P 2_1/n \) unit cell. The quinaldinate of 2a are non-planar with the twist angle of 11.4(2)°, whereas those of 2b are nearly planar. The structures of both feature...
the OH···OOC and the NH$_3^+$···OOC synthons. In 2a, a weak interaction occurs between NH$_3^+$ and OH groups. Once again, in neither of the two structures, the quinaldinate nitrogen is engaged in stronger intermolecular interactions. Its shortest contact occurs with the NH$_3^+$ group with the corresponding N···N distance being 3.1669(16) Å (2a) or 3.080(3) Å (2b). Hydrogen bonds link cations and anions into layers (polymorph 2a, Figure 3) or into chains (polymorph 2b, Figure 4). In 2a, significant π···π stacking interactions occur between quinaldinates from adjacent layers (Figure S5). Parameters of the shortest π···π stacking interaction are Ph···Py type, dihedral angle = 0.39(7)°, Cg···Cg = 3.5163(9) Å, and shift distance = 1.123 Å. The packing of chains in 2b is such that no π···π stacking occurs.
a triclinic \( P \) \(-1 \) cell was labeled 3b. The quinaldinates of the 3a polymorph are non-planar with the twist angle of 25.48(10)°. Apart from the usual synthons, the \( \text{NH}_{3}^+ \cdots \text{OOC} \) hydrogen bond, there is a short contact between the hydroxyl group of the 2a2m1pOH\( \text{H}^+ \) cation and the quinaldinate nitrogen with the O\( \cdots \)N distance being 2.8187(17) Å. The \( \text{NH}_{3}^+ \cdots \text{OOC} \) and the OH\( \cdots \text{N(quin)}^- \) hydrogen bonds link ions into chains, which propagate along a crystallographic axis (Figure 5). The chains pack in a parallel fashion without any \( \pi \cdots \pi \) stacking interactions.

\[ \text{Figure 5. Section of a chain in 3a.} \]

The 3b polymorph also consists of infinite chains. The chains propagate along \( b \) crystallographic axis. Yet, the hydrogen bonding motif markedly differs from that in 3a. Firstly, the quinaldinate nitrogen is engaged in weak interaction with the adjacent \( \text{NH}_{3}^+ \) moiety. The corresponding N\( \cdots \)N contact is 3.1037(14) Å. In the infinite chain, the following synthons may be recognized: in addition to the usual \( \text{NH}_{3}^+ \cdots \text{OOC} \) and \( \text{OH} \cdots \text{OOC} \) hydrogen bonds, there is also the \( \text{NH}_{3}^+ \cdots \text{OH} \) hydrogen bond that links the cations (Figure 6). Of the two polymorphs, only 3b displays hydrogen-bonding interactions between the cations. The packing of the chains is such that it allows \( \pi \cdots \pi \) stacking interactions between neighboring chains (Figure S6). The quinaldinates are again non-planar with the 17.26(9)° twist angle.

Products obtained upon a direct reaction of a specific amino alcohol and quinaldic acid may be classified as salts. The combinations involving amines and carboxylic acids do not always produce salts. The frequently employed \( \Delta \text{pK}_a \) rule in predicting the nature of the product [18], ionic (a salt) or neutral (a co-crystal), can give indefinite answers. It has been stated that with the difference between the pK\textsubscript{a} values that do not fall into the \(-1 \) to 4 domain, the ionization of functional groups depends upon the whole crystal packing [18], and the product classification depends upon the position of the proton along a \( \text{N} \cdots \text{O} \) hydrogen bond [19]. The combinations of amino alcohols, used in place of amines, and quinaldic acid (quinoline-2-carboxylic acid) result in the \( \Delta \text{pK}_a \) values that do not fall into the \(-1 \) to 4 domain. Although the hydroxyl group lowers the pK\textsubscript{a} value relative to the “parent” alkylamine (For example, pK\textsubscript{a} of 2-aminoethanol is by 1.15 unit lower than pK\textsubscript{a} of ethylamine, 9.50 vs. 10.65 [20]), it is the quinaldic acid that swings the balance in favor of the salt formation. The salt formation was further confirmed for all title compounds in the process of structure refinement by the location of proton in the electron difference maps.
Yet, each structure thus presents a specific situation and as such conforms with the current opinion in the field of crystal engineering that it is impossible to predict all molecular recognition events during the crystallization procedure. Firstly, the solid-state structures of title compounds, all good proton donors and acceptors are used in the intermolecular connectivity. All five structures conform to the predicted synthon hierarchy [2]: only the heterosynthons may be displayed and no homomeric ones. As shown in Table 3, all our salts feature the NH$_3^+$⋯−OOC synthon. The second one in the order of occurrence is the OH⋯−OOC synthon, which is observed in all but 3a. Interestingly, its formation is with no exception accompanied by a weak NH$_3^+$⋯N(quin$^-$) interaction. The 3a salt, which lacks the OH⋯−OOC interaction, also lacks the NH$_3^+$⋯N(quin$^-$) interaction. The absence of the NH$_3^+$⋯N(quin$^-$) interaction in 3a is compensated by the OH⋯N(quin$^-$) hydrogen bond. The salt 3a is the only compound that demonstrates this type of hydrogen bond; 3b, the other (2a2m1pOH)quin polymorph, also displays a specific feature, a NH$_3^+$⋯OH interaction. The latter is of interest because it occurs between ions of the same type, i.e., the 2a2m1pOH$^+$ cations. The survey reveals that 1 and 2b feature the same heterosynthons. The same observation pertains to the 2a/3b pair. The 3a polymorph differs from the other four structures. According to the literature, each pair of polymorphs, the 2a/2b polymorphs and the 3a/3b polymorphs, with differences in hydrogen bonding between their components may be thus classified as hydrogen bond isomers of the same solid [21]. The 2a/2b polymorphs crystallized from the same reaction mixture, as opposed to the 3a/3b polymorphs, which crystallized from different reaction mixtures. The 2a/2b polymorphs are therefore concomitant polymorphs [22]. The structures of 2a and 2b reveal another important difference. Whereas 2a features $\pi$⋯$\pi$ stacking of quinaldines, this type of interaction is lacking in 2b. The same difference pertains to the 3a/3b pair. On the other hand, the structures of all four share a common feature: the C–H⋯$\pi$ type interactions.

The structures of 1–3b have some structural features in common. The observed differences are a result of a complex interplay of short- and long-range intermolecular interactions that govern the supramolecular assembly during the crystallization procedure. Yet, each structure thus presents a specific situation and as such conforms with the current opinion in the field of crystal engineering that it is impossible to predict all molecular recognition events during the crystallization.
3. Materials and Methods

**General.** All reagents but acetonitrile were obtained from commercial sources (Aldrich and Fluorochem) and used as received. Acetonitrile was dried over molecular sieves [23]. In the case of the 2-amino-1-butanol reagent, a racemic mixture was used. The copper starting material, [Cu(quin)$_2$(H$_2$O)], was synthesized as previously reported [24]. Infrared (IR) spectra were recorded with the ATR module in the 4000–400 cm$^{-1}$ spectral range on a Bruker Alpha II FT-IR spectrophotometer (Bruker, Manhattan, MA, USA). No corrections were made to the spectra. The spectra of all reveal strong bands in the 1560–1520 and 1370–1360 cm$^{-1}$ spectral regions, which may be assigned as the $\nu_{as}$(COO$^-$) and $\nu_s$(COO$^-$) absorptions of the ionized quinoidal. The engagement of the OH and NH$_3^+$ functional groups in hydrogen bonding prevents unambiguous identification of the stretching/deformation bands of these functional groups. $^1$H nuclear magnetic resonance (NMR) spectra were recorded at 500 MHz on a Bruker Avance III 500 (Bruker BioSpin GmbH, Rheinstetten, Germany). The solvent was (CD$_3$)$_2$SO (DMSO-$d_6$) containing 0.03% tetramethylsilane (TMS), and all spectra were referenced to the central peak of the residual resonance for DMSO-$d_6$ at 2.50 ppm [25]. $^1$H NMR spectra were processed using the MestReNova program [26]. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Multiplicities are labeled as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, and m = multiplet. Elemental analysis CHN was performed on a Perkin-Elmer 2400 II analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical X’Pert PRO MD diffractometer (PANALYTICAL, Almelo, The Netherlands) using monochromatised Cu-K$_\lambda$ radiation ($\lambda = 1.5406$ Å). Thermogravimetric analyses were performed on a Mettler Toledo TG/DSC 1 instrument (Mettler Toledo, Schwerzenbach, Switzerland). Samples were heated from 25 to 450 °C with a heating rate of 10 °C min$^{-1}$ and the furnace was purged with air at a flow rate of 50 mL min$^{-1}$. The baseline was subtracted. All three salts are stable up to about 120 °C and then the decomposition processes take place. No phase transitions were observed in the 25–120 °C temperature range.

**(3a1pOH)quin (1).** Quinoidal acid (100 mg, 0.58 mmol) and acetonitrile (10 mL) were added to an Erlenmeyer flask. The mixture was stirred until all the solid was consumed. The resulting solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1). Single crystals of 1 were obtained as follows. A Teflon container was filled with CuO (50 mg, 0.63 mmol), quinoidal acid (120 mg, 0.69 mmol), acetonitrile (7.5 mL), and 3-amino-1-propanol (88 µL). The container was closed and inserted into a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. Black solid was filtered off, and the resulting green filtrate was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1). Single crystals of 1 were obtained as follows. A Teflon container was filled with CuO (50 mg, 0.63 mmol), quinoidal acid (120 mg, 0.69 mmol), acetonitrile (7.5 mL), and 3-amino-1-propanol (150 mg). The container was closed and inserted into a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. Black solid was filtered off, and the resulting green filtrate was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1).

**(3a1pOH)quin (1).** Quinoidal acid (100 mg, 0.58 mmol) and methanol (10 mL) were added to an Erlenmeyer flask. The mixture was stirred until all the solid was consumed. The resulting solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1). Single crystals of 1 were obtained as follows. A Teflon container was filled with CuO (50 mg, 0.63 mmol), quinoidal acid (120 mg, 0.69 mmol), acetonitrile (7.5 mL), and 3-amino-1-propanol (150 mg). The container was closed and inserted into a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. Black solid was filtered off, and the resulting green filtrate was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1). Single crystals of 1 were obtained as follows. A Teflon container was filled with CuO (50 mg, 0.63 mmol), quinoidal acid (120 mg, 0.69 mmol), acetonitrile (7.5 mL), and 3-amino-1-propanol (150 mg). The container was closed and inserted into a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. Black solid was filtered off, and the resulting green filtrate was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1). Single crystals of 1 were obtained as follows. A Teflon container was filled with CuO (50 mg, 0.63 mmol), quinoidal acid (120 mg, 0.69 mmol), acetonitrile (7.5 mL), and 3-amino-1-propanol (150 mg). The container was closed and inserted into a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. Black solid was filtered off, and the resulting green filtrate was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (3a1pOH)quin were filtered off. Yield: 106 mg, 74%. Notes. The identity of the product was confirmed by PXRD (Figure S1).
all the solid was consumed. The resulting solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless, needle-like crystals of (2a1bOH+H)quin were filtered off. Yield: 116 mg, 77%. Notes. PXRD confirmed that the product is mostly 2b polymorph (Figure S2). Single crystals of 2a and 2b polymorphs were obtained as follows. [Cu(quin)2(H2O)] (50 mg, 0.12 mmol), nitromethane (7.5 mL) and 2-amino-1-butanol (0.25 mL) were added to an Erlenmeyer flask. The mixture was stirred thoroughly until all the solid was consumed. After a few days, a mixture of crystals of 2a and 2b polymorphs was obtained. 1H NMR (500 MHz, DMSO-d6 with 0.03% v/v TMS): δ 8.30 (1H, d, J = 8.4 Hz, quin−), 8.08 (1H, d, J = 8.5 Hz, quin−), 8.00 (1H, d, J = 8.4 Hz, quin−), 7.95 (1H, dd, J = 8.1, 1.4 Hz, quin−), 7.76–7.72 (1H, m, quin−), 7.60–7.57 (1H, m, quin−), 3.64 (1H, dd, J = 11.7, 3.8 Hz, 2a1bOH+), 3.50 (1H, dd, J = 11.7, 6.2 Hz, 2a1bOH+), 3.04–2.99 (1H, m, 2a1bOHH+), 1.62–1.53 (2H, m, 2a1bOHH+). Elemental analysis calcld. for C14H14N2O3 (%): C, 64.11; H, 6.92; N, 10.68. Found (%): C, 64.06; H, 6.68; N, 10.77. IR of 2a polymorph (ATR, cm−1): 3017w, 2965m, 2935m, 2873m, 2752m, 2635m, 2072w, 1954s, 1576s, 1554s, 1501s, 1462s, 1428m, 1371vvs, 1346s, 1306m, 1288w, 1272w, 1254m, 1219w, 1205m, 1171s, 1151m, 1133m, 1111w, 1066s, 1041s, 988s, 967w, 953m, 980w, 958w, 946w, 912w, 893m, 873m, 853m, 804s, 778vvs, 1482m, 1467s, 1426m, 1385vs, 1372w, 1345s, 1327m, 1299m, 1264m, 1213w, 1173s, 1148m, 1114m, 1095m, 1067w, 1009w, 980w, 958w, 946w, 912w, 893m, 873m, 853m, 804s, 778vvs, 752s, 737s, 697m, 651m, 630s, 592s, 551m, 523m, 480m, 459vvs, 421m. IR of 2b polymorph (ATR, cm−1): 3232w, 3063m, 2963m, 2936m, 2868m, 1590m, 1553s, 1519s, 1503s, 1459s, 1427m, 1388s, 1367vs, 1340s, 1253w, 1219w, 1205m, 1170m, 1148m, 1068s, 1011w, 973w, 954w, 917w, 892m, 863s, 811s, 787vvs, 753m, 689m, 627s, 596s, 543w, 520m, 506m, 479w, 455w.

(2a2m1pOH)quin (3). Quinaldinic acid (100 mg, 0.58 mmol), methanol (10 mL), and 2-amino-2-methyl-1-propanol (108 µL) were added to an Erlenmeyer flask. The mixture was stirred until all the solid was consumed. The resulting solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (2a2m1pOH)quin were filtered off. Yield: 111 mg, 73%. Notes. PXRD confirmed that the product is mostly 3b polymorph (Figure S3). Single crystals of 3a polymorph were obtained as follows. [Cu(quin)2(H2O)] (50 mg, 0.12 mmol), acetonitrile (7.5 mL), and 2-amino-2-methyl-1-propanol (0.5 mL) were added to an Erlenmeyer flask. The mixture was stirred thoroughly until all the solid was consumed. The resulting blue solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a rotary evaporator. A glass vial with diethyl ether was carefully inserted into the Erlenmeyer flask with the concentrate. Colorless crystals of (2a2m1pOH)quin were filtered off. Yield: 111 mg, 73%. Notes. PXRD confirmed that the product is mostly 3b polymorph (Figure S3). Single crystals of 3a polymorph were obtained as follows. [Cu(quin)2(H2O)] (50 mg, 0.12 mmol), nitromethane (7.5 mL) and 2-amino-1-butanol (0.25 mL) were added to an Erlenmeyer flask. The mixture was stirred thoroughly until all the solid was consumed. The resulting blue solution was left to stand at ambient conditions. On the following day, it was concentrated under reduced pressure on a steel autoclave, which was heated for 24 h at 105 °C. Afterwards, the reaction mixture was allowed to cool slowly to room temperature. The resulting blue solution was left to stand at ambient conditions. After a few days, a mixture of colorless, needle-like crystals of 3b polymorph and blue crystalline solid syn-[Cu(quin)2(2a2m1pO)] was obtained. 1H NMR (500 MHz, DMSO-d6 with 0.03% v/v TMS): δ 8.30 (1H, d, J = 8.4 Hz, quin−), 8.10 (1H, d, J = 8.5 Hz, quin−), 8.01 (1H, d, J = 8.4 Hz, quin−), 7.94 (1H, dd, J = 8.1, 1.4 Hz, quin−), 7.75–7.72 (1H, m, quin−), 7.60–7.57 (1H, m, quin−), 3.43 (s, 2H, 2a2m1pOH+), 1.22 (s, 6H, 2a2m1pOH+). Elemental analysis calcld. for C14H18N2O3 (%): C, 64.11; H, 6.92; N, 10.68. Found (%): C, 63.97; H, 6.64; N, 10.71. IR of 3a polymorph (ATR, cm−1): 3185w, 2980m, 2894m, 2829s, 2724m, 2633m, 2593m, 2543m, 2168w, 1630s, 1578s, 1549w, 1503m, 1482m, 1467s, 1426m, 1385vs, 1372w, 1345s, 1327m, 1299m, 1264m, 1213w, 1173s, 1148m, 1114m, 1095m, 1067w, 1009w, 980w, 958w, 946w, 912w, 893m, 873m, 853m, 804s, 778vvs, 752s, 737s, 697m, 651m, 630s, 592s, 551m, 523m, 480m, 459vvs, 421m. IR of 3b polymorph (ATR, cm−1): 3173w, 3010m, 2965m, 2935m, 2873m, 2752m, 2635m, 2072w, 1954s, 1576s, 1554s, 1501s, 1462s, 1428m, 1371vvs, 1346s, 1306m, 1288w, 1272w, 1254m, 1219w, 1205m, 1171s, 1151m, 1133m, 1111w, 1066s, 1041s, 988s, 967w, 953m, 980w, 958w, 946w, 912w, 893m, 863s, 811s, 787vvs, 753m, 689m, 627s, 596s, 543w, 520m, 506m, 479w, 455w.
X-ray diffraction analysis. Agilent SuperNova diffractometer (Agilent Technologies XRD Products, Oxfordshire, UK) with molybdenum (Mo-Kα, λ = 0.71073 Å) micro-focus sealed X-ray source was used to obtain X-ray diffraction data on single crystal at 150 K. The diffractometer was equipped with mirror optics and an Atlas detector. The crystals were placed on a glass fiber tip with silicon grease, which was mounted on the goniometer head. CrysAlis PRO [27] was used for data processing. Structures were solved with Olex2 software [28] using intrinsic phasing in ShelXT [29] and refined with the least squares method in ShelXL [30]. Anisotropic displacement parameters were determined for all non-hydrogen atoms. With the exception of 2b, NH₃⁺ and OH hydrogen atoms of protonated amino alcohols were located from a difference Fourier map and refined with isotropic displacement parameters. Owing to the residual density in 2b, the hydrogen atoms of NH₃⁺ moiety were added in calculated positions. The remaining hydrogen atoms were placed in geometrically calculated positions in all structures and refined using riding models. Crystal structure analysis was performed with the program Platon [31], while the figures were made with Mercury [32]. The crystallographic data are summarized in Table 4. All crystal structures were deposited to the Cambridge Crystallographic Data Center (CCDC) and were assigned deposition numbers 2100261 (1), 2100262 (2a), 2100263 (2b), 2100264 (3a), and 2100265 (3b). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 15 October 2021) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 4. Crystallographic data for 1–3b.

|     | 1  | 2a | 2b  | 3a  | 3b  |
|-----|----|----|-----|-----|-----|
| **Empirical Formula** | C_{13}H_{16}N_{2}O_{3} | C_{14}H_{18}N_{2}O_{3} | C_{14}H_{18}N_{2}O_{3} | C_{14}H_{18}N_{2}O_{3} | C_{14}H_{18}N_{2}O_{3} |
| **Formula Weight** | 248.28 | 262.30 | 262.30 | 262.30 | 262.30 |
| **Crystal System** | triclinic | monoclinic | monoclinic | monoclinic | triclinic |
| **Space Group** | P ̅ – 1 | P 2 1 / n | P 2 1 / n | P 2 1 / n | P – 1 |
| **T (K)** | 150.00(10) | 150.00(10) | 150.00(10) | 150.00(10) | 150.00(10) |
| **λ (Å)** | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **a (Å)** | 7.1378(16) | 12.1437(11) | 6.5579(4) | 6.5428(4) | 7.1342(4) |
| **b (Å)** | 7.5269(7) | 10.1451(5) | 10.2309(6) | 9.0723(4) | 8.4346(3) |
| **c (Å)** | 11.8314(14) | 12.2312(15) | 19.8329(13) | 23.1232(10) | 12.5059(7) |
| **α (°)** | 99.172(9) | 90 | 90 | 90 | 96.139(4) |
| **β (°)** | 95.916(14) | 119.527(14) | 97.837(6) | 93.835(5) | 105.187(5) |
| **γ (°)** | 90.647(13) | 90 | 90 | 90 | 104.829(4) |
| **V (Å³)** | 623.93(17) | 1311.2(3) | 1318.22(14) | 1369.48(12) | 689.74(6) |
| **Z** | 2 | 4 | 4 | 4 | 2 |
| **D_{calc} (g/cm³)** | 1.322 | 1.329 | 1.322 | 1.272 | 1.263 |
| **µ (mm⁻¹)** | 0.095 | 0.094 | 0.094 | 0.090 | 0.090 |
| **Collected Reflections** | 5349 | 11,880 | 6877 | 12,825 | 12,006 |
| **Unique Reflections** | 3186 | 3524 | 3413 | 3696 | 3689 |
| **Observed Reflections** | 1937 | 2780 | 2459 | 2528 | 2933 |
| **R_{int}** | 0.0587 | 0.0285 | 0.0233 | 0.0482 | 0.0224 |
| **R_{1} (I > 2σ(I))** | 0.0878 | 0.0413 | 0.0671 | 0.0513 | 0.0429 |
| **wR_{2} (all data)** | 0.2559 | 0.1168 | 0.2000 | 0.1225 | 0.1274 |

4. Conclusions

Reactions of amino alcohols (3-amino-1-propanol, 2-amino-1-butanol, or 2-amino-2-methyl-1-propanol) and quinaldinic acid have produced salts, which consist of protonated amino alcohol and deprotonated quinaldinic acid. The obtained products obey the ΔpKₐ rule. Of the three products, (3a1pOH)quin (1), (2a1bOH)quin (2), and (2a2m1pOH)quin (3), the last two are polymorphic. A structural survey has revealed all
five possible heterosynthons in their crystal structures. The supramolecular structures of all are built of the NH$_3^+$···OOC synthon in combination with one to up to three other heterosynthons. Interestingly, the OH···N(quin−) synthon occurs only in one phase. The 2a/2b and 3a/3b polymorphic pairs differ both in the types of hydrogen bonds and in π···π stacking interactions. Due to the former, they are hydrogen bond isomers of the same compound. The presented series is yet another demonstration of polymorphism among molecular solids.

Supplementary Materials: The following supporting information can be downloaded, PXRD patterns (Figures S1–S3), packing diagrams (Figures S4–S6), IR spectra for 1–3b (Figures S7–S11), 1H NMR spectra for 1–3 (Figures S12–S14), and TG/DSC curves (Figures S15–S17).

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