ORIGINAL RESEARCH

Organic mandelates as promising materials with non-linear optical application

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Abstract The application of organic salts of mandelic acid (MA) as new materials for optical and non-linear-optical (NLO) application is discussed, using four novel organic salts, i.e. pyridinium-4-aldoxime mandelate (1), 1-amino-isoquinolinium mandelate mandelic acid (2), 2-amino-8-hydroxyquinolinium mandelate (3) and phenylalaninamide mandelate monohydrate (4). The crystal structures, optical and NLO properties are studied by the application of single crystal X-ray diffraction, UV–VIS–NIR spectroscopy, conventional and linear polarized infrared (IR-LD) spectroscopy, thermal methods as well as quantum chemical (ab initio and DFT) calculations.

Keywords Organic mandelate crystals · Optical and NLO properties

Introduction

The design of non-linear optical devices incorporating second harmonic generator materials, which produce frequency

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M. Spiteller e-mail: spiteller@infu.tu-dortmund.de doubling effect of optical wavelength electromagnetic radiation, is attractive area of modern materials research and crystal engineering [1-10]. It is known that various organic and inorganic compounds possess the ability to double the frequency of laser light passing through them, this ability is known as SHG and provides the ability to produce laser light of higher energy than that provided by the initial laser light source. Known organic compounds, possessing such properties are for example urea, cadmium-thiourea complexes, L-arginium dihydrogen phosphate monohydrate, some siloxane and silicone polymeric liquid crystals, stilbenecontaining liquid crystals, some silver-containing emulsions, dipotassium tartrate hemihydrate, potassium sodium tartrate tetrahydrate, compounds having large secondary molecular susceptibilities (beta-values) such as 4-(N-pyrrolidino)-3-(N-ethanamido)-nitrobenzene and 4-(dimethylamino)-3-(N-ethanamido)-nitrobenzene, and blends of large beta-value compounds with polypeptides [11]. The organic salts of mandelic acid (MA) are especially attractive templates for incorporation into crystalline materials with NLO properties, because of the presence of an additional OHgroup to the carboxylic one, promotes hydrogen bonding with the base. Hydrogen bonding also tends to increase the thermal stability and mechanical strength of the crystalline material, and to suppress the formation of crystalline hydrates. The corresponding organic base is preferably an amine, imine [1-4, 11-15] or heterocycle with basic nitrogen atoms. For these reasons the current research is focused on design, synthesis and isolation of the organic mandelates (Scheme 1). Their spectroscopic properties and structures are elucidated by conventional and IR-LD spectroscopy, UV-VIS-NIR, thermal methods and single crystal X-ray diffraction. The optical and NLO optical properties are predicted by application of quantum chemical calculations at ab initio and DFT levels of approximation.

Scheme 1 Pyridinium-4aldoxime mandelate (1), 1-aminoisoquinolinium mandelate mandelic acid (2), 2-amino-8-hydroxyquinolinium mandelate (3) and phenylalaninamide mandelate monohydrate (4)



Results and discussion

Pyridinium-4-aldoxime mandelate (1) crystallizes in the non-centrosymmetric tetragonal P43 space group (Fig. S1a) indicating NLO properties in the bulk. The unit cell contains 16 species, forming a 3D network (Fig. 1a) by means of moderate to strong N⁺H···O, OH···OCO hydrogen bonds (2.706, 2.605 Å). The MA anions form dimers via OH…OCO bonds (2.759, 2.792 Å). 1-Aminoisoquinolinium mandelate mandelic acid (2) crystallizes in a triclinic $P\bar{1}$ space group (Fig. S1b). The structure consists of cationic 1-aminoisoquinoline, mandelate anion and neutral MA (Fig. 1b). The weak basic character of the 1-amino substituent limits the protonation of the NH₂ group in the presence of the second molecule MA. As with (1), the MA species forms dimers through OH…OCOH (2.878 Å) bonds. Each of the latter sub-structures is joined into infinite chains through OH…OCO (2.566 Å) bonds (Fig. 1b). The cations interact with the MA species by N⁺H···O hydrogen bonds (2.912, 3.011, 2.777 Å). 2-Amino-8hydroxyquinolinium mandelate (3) crystallizes in a monoclinic $P2_1/c$ space group (Fig. S1c). The cations and MA anions form 3D networks via NH…O (2.740, 3.016, 2.900 Å) and OH…OCO (2.471, 2. 962 Å) interactions (Fig. S1c). The sub-structural fragment of the MA anion is an isolated moiety. As with 1-aminoisoquinoline and its monocation, the weak basic character of the NH₂-group limits the formation of the dication (Scheme S1) with excess MA. The NH₂-group takes part in the conjugation with the quinoline fragment, thus leading to a singly charged redistribution value of -0.842 in the neutral species and -0.756 in corresponding cation (Scheme S1). Phenylalaninamide mandelate monohydrate (4), crystallizes in the non-centrosymmetric space system C2, supposing NLO properties in the bulk (Fig. S1d). The selfassembly motif of the mandelate is infinite chains, formed by means of the OH…OCO hydrogen bonds (2.805 Å). The cations are joined by the anions and the solvent molecules through the moderately strong intermolecular NH---O hydrogen bonds (3.026, 2.776, 2.815, 2.840, 3.042 Å)





Fig. 2 Solid-state IR spectra of noncentrosymmetric crystals (1)-(4)

(Fig. 1d). The experimental crystallographic refinement data are summarized in Table S1.

The solid-state IR spectra of compounds (1)-(4) are depicted in Fig. 2. The characteristic multicomponent maximum within 3100-3000 cm⁻¹ in all IR-spectra is assigned to the v_{OH} stretching vibration of the hydrogen bonded OH-group. The IR-bands about at 1550 and 1400 $\rm cm^{-1}$ belong to the $\nu^{as}_{\rm COO-}$ and $\nu^{s}_{\rm COO-}$ vibrations of the MA anion, respectively. IR-spectrum of (2), shows a band of $v_{C=0}$ vibration at 1724 cm⁻¹ (Fig. 3(2)) of the protonated COOH group of the neutral MA. The IR-bands at 3454 and 3378 cm⁻¹ can be assigned to the corresponding v_{OH} vibrations. In contrast to local C_{2v^*} symmetry of the carboxylate anion (COO⁻), characterizing the redistribution of the negative charge, the neutral COOH group reveals a typical C=O bond and the local C_s symmetry. The values of the C–O bonds in the MA anion in (2) are 1.263, 1.244 Å, while the corresponding values in the neutral acid are 1.206 and 1.300 Å, respectively. The characteristics out-of-plane IR bands of the monosubstituted benzene ring in MA species are observed at about 760, 730 and 690 cm⁻¹ (Fig. 2(1)-(4)). The cationic fragments in (2) and (3) are characterized by C_s molecular symmetry of the neutral and protonated forms (Scheme S1). The corresponding IR spectra reveal out-of-plane maxima within the range 960–600 cm^{-1} typical for these systems (Scheme S2; Fig. S2) overlapping with those of MA moieties.

The transmission UV–VIS–NIR spectra of compounds (1)–(4) and the starting compounds within the range 190–1100 nm are depicted in Fig. 3. Neutral MA is characterized by a weak UV-band at 260 nm ($\varepsilon_v = 621 \text{ l mol}^{-1} \text{ cm}^{-1}$), belonging to B-band of the substituted benzene ring, overlapped with the $n \rightarrow \pi^*$ transition of the C=O group. The observed vibronic structure of the B band is typical for





Fig. 3 Transmission UV–VIS–NIR spectra of aqueous solution of a mandelic acid at pH 4 and 9, pyridine-aldoxime, 1-aminoisoquinoline and 2-amino-8-hydroxyquinoline; b compounds (1)–(4) at a concentration 2.10–5 mol/l and 1 cm path length

substituted phenyl-fragments [12]. These data compare with the theoretical value of 240 nm and f = 0.013. The MA anion exhibits a hypsochromic shift of the B-band and disappearance of the $n \rightarrow \pi^*$ transition as a result of distortion of the C=O double bond in the COOH-group of the neutral acid. MA is transparent within the range of 204-1100 nm. The pyridine-4-aldoxime and the substituted quinolines exhibit a series of absorption maxima at 240–290 nm with ε_{ν} within range of $800-1200 \text{ 1 mol}^{-1} \text{ cm}^{-1}$. 1-Aminoisoquinoline is characterized by the highest wavelength band at 335 nm and ε_v 1198 l mol⁻¹ cm⁻¹. These bands belong to the transitions $8A'' \rightarrow 9A''$ in the quinoline fragments (Scheme S3). The observed vibronic structure is also typical for the electronic spectra of substituted naphthalenes [12, 13] and could be analogous to quinolines. The effect of the protonation of the counterions leads to a bathochromic shift of the highest wavelength UV-bands within 15-60 nm (Fig. 3b). The compounds (1) and (4) are transparent within the larger transmission window within 280-1100 nm, while for the compounds (2) and (3) the corresponding ranges are 346-1100 nm and 353-1100 nm, respectively. The data are in accord with the theoretical values 350 and 360 nm (Scheme S3) and the f values of 0.017 and 0.023, respectively. The protonation of the quinoline derivatives leads to a decrease in the energy difference and to a bathochromic shift of the corresponding maxima. The energy values of MOs

Table 1 The	pretical UV spec	tra in aqueous s	olution of (1)-(3	3)							
B3LYP/6-31 -	$++G^{**}, \lambda \text{ [nm]}$	(f^{a})	B3PW91, λ [n	ım] (f ^a)		CAM-B3LYP,	$\lambda [\text{nm}] (f^{a})$		CAM-B3PW9.	1, λ [nm] (f^{a})	
(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
$265 \ (0.041_0)$	335 (0.0411)	344 (0.012 ₈)	265 (0.044 ₃)	335 (0.0461)	345 (0.0211)	$265 \ (0.043_7)$	335 (0.0511)	345 (0.0111)	267 (0.037 ₈)	340 (0.0201)	355 (0.021 ₁)
MO5, λ [nm]	(f ^a)		MO5-2X, λ [n	um] (f ^a)		MO6, <i>λ</i> [nm]	(f ^a)		M06-2X XC,	$\lambda \; [nm] \; (f^a)$	
(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
280 (0.0393)	350 (0.0489)	360 (0.0232)	282 (0.042 ₃)	350 (0.045 ₆)	360 (0.0211)	$283 (0.040_0)$	350 (0.0202)	360 (0.0231)	285 (0.051 ₂)	350 (0.017 ₂)	360 (0.0231)
^a f oscillator i	strenoth										

8A'' and 9A'' in the cation of 2-amino-8-hydroxyquinoline are -3.079 and 0.3682 eV (MO6-2X XC, Table 1).

Calculations at MO5, MO5-2X, MO6 and MO6-2X XC functional levels were performed and complete the elucidation of the electronic spectra of the systems (1)-(3)[16–18]. The data are summarized in Table 1. As with the calculation of the optical properties of small L-tryptophancontaining peptides or NLO materials based on barbiturate salts [19, 20] the DFT approximation at B3LYP level of theory, yielded serious shortcomings. The so-called M06class functional [16-18] was used to enforce some fundamental exact constraints yielding a good correlation between the theoretical and the experimental values. The data show that M06 has good accuracy for medium-range correlation energy as has M06-2X, which has excellent predicts accurate valence and Rydberg electronic excitation energies. For the systems (1)-(3), the differences between the theoretical and the experimental electronic spectra are in the range within 3-7 nm, thus indicating the good correlation for the substituted heterocyclics.

Conclusions

The search for new organic materials with NLO properties on the basis of the salts of mandelic acid provided encouraging results, yielding four novel derivatives; pyridinium-4aldoxime mandelate (1), 1-aminoisoquinolinium mandelate mandelic acid (2), 2-amino-8-hydroxyquinolinium mandelate (3) and phenylalaninamide mandelate monohydrate (4). The structures and optical properties of compounds (1)-(4) are elucidated by single crystal X-ray diffraction, UV–VIS-NIR, IR-LD spectroscopy and thermal methods. The theoretical quantum chemical calculations were carried out to predict the optical properties of these systems. Compounds (1) and (4) crystallize in the non-centrosymmetric space groups $P4_3$ and C2, thus indicating the NLO properties in the bulk. Mandelic acid species form dimers in (1) by the OH…OCO bonds (2.759, 2.792 Å) and infinite chains in (4) by OH…OCO bonds (2.805 Å), respectively. Compounds (2) and (3) crystallize in the triclinic $P\bar{1}$ and monoclinic $P2_1/c$ space groups, respectively. The selfassembly sub-structures of the mandelic acid species are dimers (OH…OCOH, 2.878 Å) in (2) and isolated anion in (3), respectively. Instead that compounds (1) and (4) crystallized in non-centrosymmetric space groups, the properties of these crystals are such as to include some of the most important characteristic desired for practical application in useful for crystal engineering and NLO technology. The compounds are characterized by high solubility in aqueous media, allowing reasonable rate of crystal growth and good properties, particularly in the cases of (1) and (4). The compounds possess high thermal stability at temperatures

higher than 500 °C, neither are they hygroscopic. All the crystals are colourless and posses a large transmission window with a range 260–1100 nm as well as low intensive IR bands within the range 5000–400 cm⁻¹. Compound (1) forms hydrate-free crystals, thus avoiding the evaporation of water and degradation under prolonged exposure to laser radiation.

Experimental

Synthesis

Pyridinium-4-aldoxime mandelate (1), 1-aminoisoquinolinium mandelate mandelic acid (2), 2-amino-8-hydroxyquinolinium mandelate (3) and phenylalaninamide mandelate monohydrate (4) were obtained by mixing equimolar amounts of the pyridine-4-aldoxime mandelate (0.1231 g), 1-aminoisoquinoline (0.1150 g), 2-amino-8-(0.5671 g) hydroxyquinoline or phenylalaninamide (0.3141 g) with 0.4575 g mandelic acid (all Sigma-Aldrich products) in 20 ml methanol/water 1:1 at under stirring for 30 min at 150 °C. The resulting colourless crystals (Fig. 1) were filtered off, washed with CH₃OH and dried on P₂O₅ at 298 K. Yields 91 (1), 43 (2), 66 (3) and 89 (4)%, respectively. Found (1): C, 61.35; H, 5.14; N, 10.28; calcd. for C₁₄H₁₄O₄N₂: C, 51.31; H, 5.14; N, 10.21%. Found (2): C, 67.35; H, 5.17; N, 6.28; calcd. for C₂₅H₂₃O₆N₂: C, 67.11; H, 5.18; N, 6.26%. Found (3): C, 65.35; H, 5.14; N, 8.98; calcd. for C17H16O4N2: C, 65.38; H, 5.16; N, 8.97%. Found (4): C, 62.99; H, 6.27; N, 8.68; calcd. for C₃₄H₄₀O₉N₄: C, 62.95; H, 6.22; N, 8.64%. Thermal analysis applied to (1)-(4) over the range 0-500 °C confirmed the crystallographic data for the presence or absence of the solvent molecules in the compounds.

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References

- Koleva B, Kolev T, Seidel R, Spiteller M, Mayer-Figge H, Sheldrick W (2009) J Phys Chem 113A:3088
- Koleva B, Kolev T, Seidel R, Mayer-Figge H, Spiteller M, Sheldrick W (2008) J Phys Chem 112A:2899
- 3. Ivanova B, Spiteller M (2010) J Phys Chem A 114:5099
- 4. Karle I, Ranganathan D, Haridas V (1996) J Am Chem Soc 118:7128
- 5. Gilli G, Bertolasi V, Gilli P, Ferretti V (2001) Acta Crystallogr B57:859
- Bosshard Ch, Hulliger J, Florsheimer M, Günter P (2001) Organic nonlinear optical materials, advances in nonlinear optics. Gordon and Breach Science Publishers SA, Postfach, Basel
- Chemla D, Zyss J (1987) In: Chemla D, Zyss J (eds) Nonlinear optical properties of organic molecules and crystals, vol 1. Academic Press, New York, pp 23–187
- Nalwa H, Watanabe T, Miyata S (1997) In: Nalwa HS, Miyata S (eds) Nonlinear optics of organic molecules and polymers. CRC Press, Boca Raton, pp 89–329
- 9. Reetz M, Hoger S, Harris K (1994) Angew Chem Int Ed 33:181
- 10. Saha BK, Nangia A, Nicoud J-F (2006) Cryst Growth Des 6:1278
- 11. Brian P (1991) USA Patent PCT/GB/91/00616, 1991
- Andrews L, Kelsall BJ, Blankenship TA (1982) J Phys Chem 86:2916
- Andrews L, Friedman RS, Kelsall BJ (1985) J Phys Chem 89: 4550
- 14. Ofir Y, Zelichenok A, Yitzchaik S (2006) J Mater Chem 16:2141
- Mebel AM, Hayashi M, Liang KK, Lin SH (1999) J Phys Chem A 103:10674
- 16. Zhao Y, Truhlar D (2008) Acc Chem Res 41:157
- 17. Schultz N, Zhao Y, Truhlar D (2008) J Comput Chem 29:185
- 18. Zhao Y, Truhlar D (2008) Theor Chem Acc 120:215
- Ivanova B, Spiteller M (2010) Biopolymers. doi:10.1002/bip.21 437
- Ivanova B, Spiteller M (2010) Cryst Growth Des. doi:10.1021/cg 100284r