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Theoretical and experimental comparative studies of nonlinear optical properties for selected melaminium compounds

Research Article

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Abstract: The bis(melaminium) sulphate dihydrate, 2,4,6-triamine-1,3,5-triazin-1,3-ium tartrate monohydrate, 2,4,6-triamine-1,3,5-triazin-1-ium hydrogenphthalate, 2,4,6-triamine-1,3,5-triazin-1-ium acetate acetic acid solvate monohydrate, 2,4,6-triamine-1,3,5-triazin-1-ium bis(selenate) trihydrate, melaminium diperchlorate hydrate, melaminium bis(trichloroacetate) monohydrate and melaminium bis(4-hydroxybenzenesulphonate) dihydrate were discovered recently as perspective materials for nonlinear optical applications. On the basis of X-ray structures for eight melaminium compounds the time dependent Hartree Fock (TDHF) method was used for calculation of the polarizability, and first and second hyperpolarizability. Detailed directional studies of calculated hyperpolarizability for all investigated melaminium compounds are shown. The theoretical results are compared with experimental values of β.

Keywords: *NLO materials • Time dependent HF • Melaminium Cation • Semi-empirical method • Hyperpolarizability*

1. Introduction

In investigations of new molecular crystals with nonlinear optical properties (NLO), two trends are observed. Traditionally, the large value of the second order NLO coefficient, β, of an organic molecule has been associated with the intramolecular charge transfer (ICT). This mechanism results from the communication between electron donor and acceptor groups through a π-conjugated molecular framework [1-3]. The second trend deals with molecules having threefold rotational axis or symmetry close to D_{3h}, C_3 or D_3 point group. Such so called octupolar molecules exhibit non-zero β, inspite of being nonpolar [4]. Therefore, molecules as well as molecular ions of those point group symmetry display desirable properties. In addition to molecules with a two-dimensional (2D) character of β, a few 3D octupolar molecules have been also investigated.

Kurtz and Perry [5] described the experimental test for efficiency of second harmonic generation (SHG). This technique uses powders and permits the rapid classification of materials according to (a) magnitude of nonlinear optical coefficients relative to standard (KDP – potassium hydrogen phosphate, urea, quartz) and (b) existence or absence of phase matching direction(s) for SHG. Results were presented for a large amount of inorganic and organic substances including single-crystal data on phase-matched second-harmonic generation *e.g.* HIO_3, $KNbO_3$, $PbTiO_3$, $LiClO_4 \cdot 3H_2O$, and $CO(NH_2)_2$. This method was successfully used for melaminium complexes, also.

Much faster for estimation of NLO properties seems to be theoretical calculation method (TDHF), but it is not clear that this method gives good results, *i.e.*, close to experimental data. The time-dependent Hartree-Fock (TDHF) approximation was introduced in atomic and molecular physics for the description of the linear response of atomic and molecular systems to an externally applied field, as well as of their excited states, both discrete and continuum [6]. As such, the method was proved to be very successful [7-12] for obtaining good approximations for atomic polarizabilities and generalized oscillator strengths, as well as for photoionization cross-sections. In the TDHF approximation, the wavefunction of the atomic (molecular) electrons is assumed to have a Slater determinant form in the presence of an external,

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time-dependent potential which is treated as fully coupled in. After obtaining the linear response function from this assumption, a model for the atomic (molecular) excited states emerges and for each excited electron, a physically meaningful potential is created.

Recently, few new compounds with melaminium cation were reported as perspective materials for nonlinear optics. Therefore, it seems to be worthwhile to have fast computational method for preliminary assesment of the value of β coefficient.

In this paper we report comparative studies of experimental and theoretical results for selected melaminium compounds. According to our investigation it is clear that semi-empirical methods can be used for evaluation of first hyperpolarizability in new molecular complexes.

2. Experimental Procedure

The previously published X-ray structural data were used for computational studies. All the structures are available under following (ConQuest Version 1.12 program; Cambridge Structural Database): CCDC 179274 (for BMSD - Bismelaminium sulphate dihydrate), Refcode AJOFUA (for MTM - melaminium tartrate monohydrate), CCDC 158283 (for MHP - melaminium phthalate), CCDC 182040 (for MAAASM - melaminium acetate acitic acid solvate monohydrate), CCDC 173437 (for MBST - melaminium bis(selenate) trihydrate), CCDC 125781 (for MDPM - melaminium diperchlorate monohydrate), CCDC 616128 (for MBTCAM - melaminium bis(trichloroacetate) monohydrate) and CCDC 169961 (for MB4HBSD - melaminium bis(4-hydroxybenzenesulphonate) dihydrate).

The coordinates for particular atoms of each molecule were taken from Crystallographic Information Files [13] (CIF) and Z-matrix was built by Molden program. The Z-matrix was directly used in input Gamess files. For calculation of equilibrium geometries of investigated complexes the semi-empirical PM3 methods was used.

The nonlinear optical response of an isolated molecule in an electric field $E_i(w)$ can be presented as a Taylor series expansion of the total dipole moment, μ_t, induced by the field:

$$\mu_t = \mu_0 + \alpha_{ij}E_i + \frac{1}{2}\beta_{ijk}E_iE_j + \ldots$$

where α_{ij} is a linear polarizibility, μ_0 is permanent dipole moment, and β_{ijk} are the first hyperpolarizability tensor components. The NLO response of the material in molecular state can be determined by computation [14] or experimentally. The definition of methodology used in our calculation for first and second hyperpolarizability was previously described [3].

For calculation of the first hyperpolarizability, quantum chemical time dependent Hartree Fock (TDHF) method was chosen.

All calculations were performed with PC GAMESS program [15], version 7.0 (Dragon), build number 3766 from 04-02-2006. This job was executed in one node sequential mode (the PM3 semi-empirical method is not implemented for parallel execution in Gamess). The NT-MPICH [16] implementation of MPI standard (Message Passing Interface) was used as cluster manager.

3. Results and Discussion

The selected main structural motifs for all investigated compounds are shown in Fig. 1. All considered x, y and z coordinates of discussed compounds originate from papers recently published [17-24]. For these compounds the theoretical calculations of NLO properties were performed. All theoretical results are given in the molecular internal coordinate system represented by (X, Y, Z) whereby the indices X, Y and Z refer to the three axes corresponding to the components of moment of inertia in increasing order.

3.1 Dipole moments and polarizability

It is clear that results of dipole moments calculations strongly depend on selected basis set [25]. The selected semi-empirical basis set seems to be insufficient for quantitative investigation of dipole moments, but on the other hand this simple basis set can be proper for fast comparison studies for similar compounds (as in our case of eight melaminium compounds).

The calculated dipole moments μ and isotropic polarizability α are collected in Table 1. In our theoretical approach the biggest dipole moments are obtained for melaminium tartrate monohydrate and melaminium phthalate. For the former compound the dipole moment is equal to 50.41 D, whereas for the latter one is 36.33 D. It should be mentioned that the highest values of calculated dipole moments were obtained for two complexes with molecular ratio 1:1 (melamine : tartrate or phthalate). The very high dipole moment was also observed for compounds with tartaric acid as main structural motif [26]. It is interesting that for melaminium tartrate monohydrate, the dipole moment obtained in theoretical approach is observed in X direction (the directions were chosen according to moment of inertia of investigated compounds, where in X direction moment of inertia is the smallest, whereas along Z direction this moment is the biggest one, see Fig. 1). In Y and Z directions dipole moment is practically negligible. Similar relationship is observed in the case of two melaminium

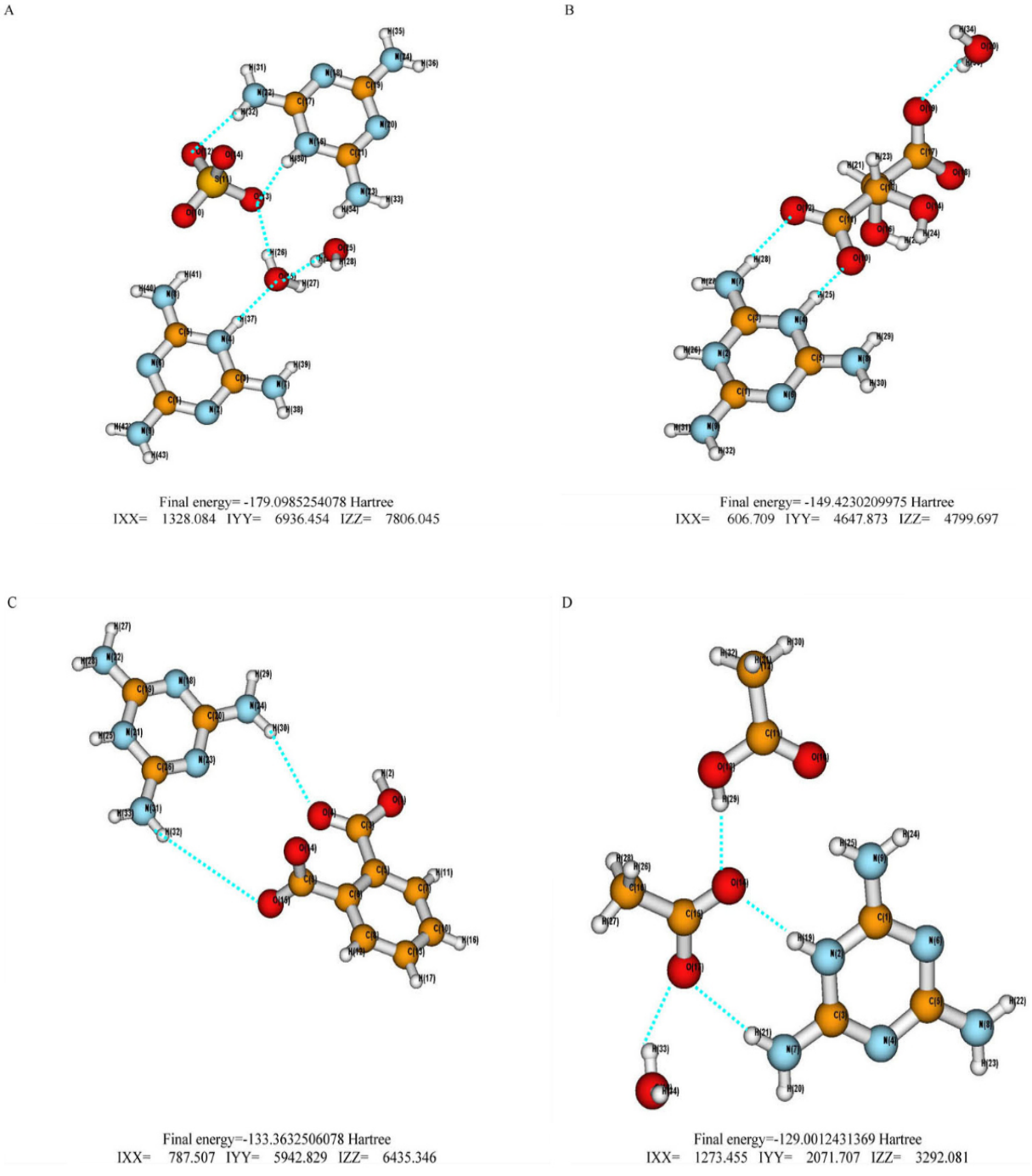
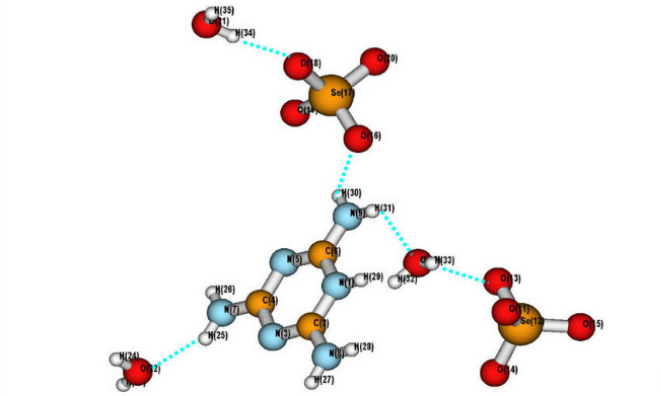


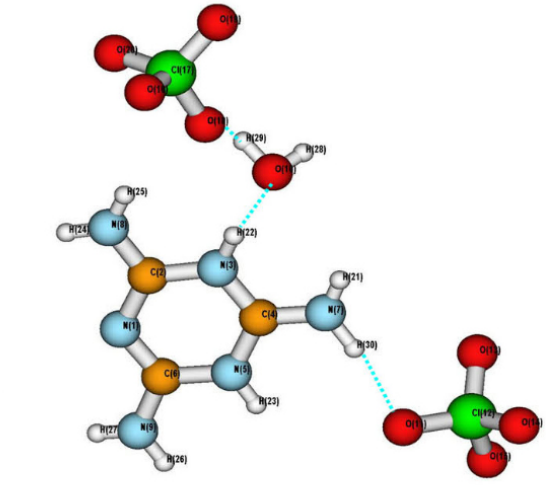
Figure 1. The structures used in calculation with length of bonds [A], energy of calculated form [Hartree]and values of moments of inertia [amu-A^2] form each molecule (a-bismelaminium sulphate dihydrate, b – melaminium tartaric acid monohydrate, c – melaminium ftalic acid, d – melaminium acetate acitic acid monohydrate)

E



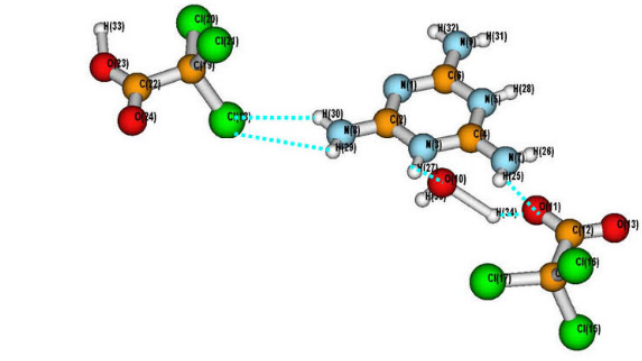
Final energy= -188.1292500994 Hartree
IXX= 3388.318 IYY= 7604.143 IZZ= 10137.000

F



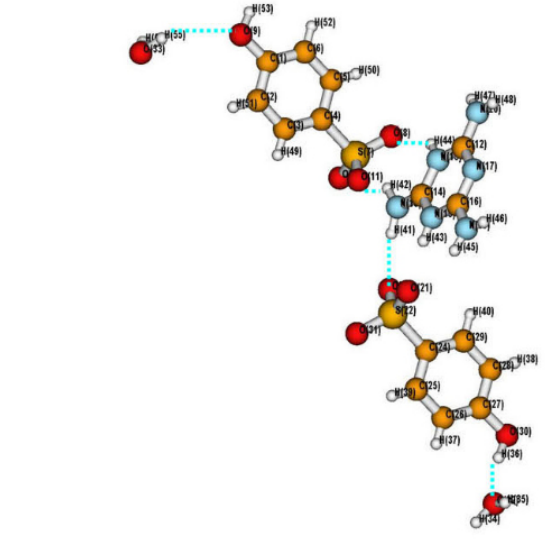
Final energy= -174.1986490157 Hartree
IXX= 1260.855 IYY= 4962.656 IZZ= 5867.915

G



Final energy= -195.2911683068 Hartree
IXX= 1531.572 IYY= 11819.478 IZZ= 12275.754

H



Final energy= -234.6914221457 Hartree
IXX= 2364.940 IYY= 13370.111 IZZ= 14854.437

Continued **Figure 1.** The structures used in calculation with length of bonds [A], energy of calculated form [Hartree]and values of moments of inertia [amu-A^2] for each molecule (e – melaminium bisselenate trihydrate, f – melaminium diperchlorate monohydrate, g – melaminium bistrichloroacetate monohydrate, h –melaminium bis(4-hydroxybenzenesulphonate) dihydrate).

Table 1. The calculated dipole moments μ [D] and polarizability α [10^9 esu cm^{-2}] for investigated molecules.

Dipole moments in Debye and polarizability	Bismelaminium sulphate dihydrate	Melaminium tartrate monohydrate	Melaminium phthalate	Melaminium acetate acetic acid solvate monohydrate
μ_X	-7.35	50.21	-27.14	-4.12
μ_Y	-15.86	-1.30	22.95	-6.55
μ_Z	-8.42	4.36	-7.52	1.98
μ	19.40	50.41	36.33	7.99
$\alpha_{average}$	3.18	3.18	2.53	2.00
Dipole moments in Debye and polarizability	**Melaminium bis(selenate) trihydrate**	**Melaminium diperchlorate monohydrate**	**Melaminium bis(trichloro-acetate) monohydrate**	**Melaminium bis(4-hydroxybenzenesulpho-natre) dihydrate)**
μ_X	3.79	1.33	8.10	-2.74
μ_Y	-9.63	19.92	12.01	21.50
μ_Z	3.80	3.99	-10.27	3.05
μ	11.03	20.36	17.76	21.89
$\alpha_{average}$	3.82	2.22	3.15	3.82

complexes, melaminium diperchlorate monohydrate and melaminium bis(4-hydroxybenzenesulphonate) dihydrate. For these complexes the highest values of dipole moments are observed along Y direction. For the remaining melaminium complexes any directional relation is affirmed.

For other three complexes, bis(melaminium) sulphate dihydrate, melaminium diperchlorate monohydrate and melaminium bis(4-hydroxybenzenesulphonate) dihydrate, the calculated values of dipole moments are equal to 20 D, approximately. For two other compounds these theoretical data are the smallest and equal to *ca.* 10 D.

In theoretical calculation the highest values of average polarizability α are obtained for two melaminium compounds, *i.e.*, with selenic and 4-hydroxybenzenesulphonic acids. For these complexes the theoretical values of α are equal to *ca.* 3.82 [10^9 esu cm^{-2}]. The medium values of polarizability were obtained for three investigated compounds (nr 1, 2 and 7 in Table 1). The calculated data of polarizability are quite similar and equal to 3.18 [10^9 esu cm^{-2}]. The smallest values of α were calculated for three other compounds (in Table 1 numbers: 3, 4 and 6). The theoretical values noticed in this case are in the range of 2.00 – 2.53 [10^9 esu cm^{-2}].

3.2 Hyperpolarizability β

The calculated values of β vector part at fundamental wavelength of 1064 nm and comparison with experimental results are shown in Table 2. The directional properties of β hyperpolarizabilty are collected in Table 3.

An experimental investigation shows clearly that only for three melaminium compounds is a significant hyperpolarizability observed. The smallest value (about 0.40 relatively to KDP) is noticed in the case of melaminium bis(selenate) trihydrate, whereas the twice more intensive second order NLO effect is observed for melaminium tartrate monohydrate. However, the strongest hyperpolarizability was detected for melaminium bis(trichloroacetate) monohydrate. In this case the β value is approximately three times stronger in relation to KDP. A non-zero β hyperpolarizabilty was not obtained for the other investigated melaminium compounds.

The theoretical results shown that for three considered compounds the β vector values are extremely small, and equal to *ca.* 5 – 10×10^{-30} [esu]. These results are obtained for melaminium phthalate, melaminium acetate acetic acid monohydrate and for melaminium diperchlorate monohydrate crystals. In this case the experimental and theoretical values are in very good agreement.

Table 2. The comparison of β vector's part of hyperpolarizability with experimental results for investigated compounds (unit of β is 10^{-30} esu).

Compounds	$\beta_{(Vector)}$	$\beta_{(experimental)}$ b(KDP=1)
Bis-(melaminium) sulphate dihydrate	55.72	0
Melaminium L-tartrate monohydrate	226.75	1
Melaminium phthalate	10.60	0
Melaminium acetate acetic acid solvate monohydrate	7.60	0
Melaminium bis-(selenate) trihydrate	24.17	0.40
Melaminium diperchlorate monohydrate	4.71	0
Melaminium bis-(trichloroacetate) monohydrate	95.87	3.09
Melaminium bis-(4-hydroxybenzenesulfonate) dihydrate	41.40	0

For two other compounds: melaminium sulphate dihydrate and melaminium bis(4-hydroxybenzenesulphonate) dihydrate complexes the experimental values of hyperpolarizabilty are negligible whereas the theoretical data are equal to 55.72×10^{-30} [esu] and 41.40×10^{-30} [esu], respectively.

A little bit bigger value of calculated hyperpolarizability is noticed for melaminium bis(selenate) trihydrate. In this case the theoretical result is equal to 24.17×10^{-30} [esu]. According to theoretical calculation the second order nonlinear effect in this compound should be evaluated as extremely weak, but experimental data show the small NLO response.

The higher β hyperpolarizability of two melaminium compounds (with tartaric acid and hydroxybenzenesulphonic acid) was confirmed by theoretical approach. However, the obtained results are different than experimental data. In the theoretical approach the highest value of β (226.75×10^{-30} [esu]) was obtained for melaminium tartrate monohydrate, while the much smaller data are calculated for compound with the highest experimental value of hyperpolarizability (melaminium bis(trichloroacetate) monohydrate). In this case the theoretical value of β is equal to 95.87×10^{-30} [esu].

The effect of smaller value for calculated hyperpolarizability than experimental one was observed [3], previously, but in the case of our work this differences are significantly greater. It is important to note that the theoretical method used here (TDHF) does not include the electron correlation effect which has been found in a number of cases as considerably influencing the NLO coefficient [27]. Additionally, recent experimental measurements and theoretical analyses reveal [28] that in the low frequency limit, the electron-phonon coupling contribution to the optical nonlinearity may become quite important. Thus, taking into account of vibronic terms in the calculation of NLO coefficients may become necessary for better agreement with experiment [3]. It should be emphasized that similar type of coupling between the high-frequency hydrogen stretching vibration and low-frequency phonons is described [29] in crystals with hydrogen bonds.

It should be mentioned that hyperpolarizability β in melaminium tartrate monohydrate is dominated by the longitudinal component β_{xxx}, whereas the medium values of β are noticed for direction YXY, XXZ, ZXX and ZXZ (Table 3). For the other directions these β values are noticed in the wide range of 0.17×10^{-30}(YYZ) – 9.28×10^{-30} (ZXY) [esu]. The dominance of the one β_{xxx} component indicates the maximum change in the induced dipole moment along this direction, which is also the charge transfer axis of the molecule.

The theoretical results obtained for melaminium bis(trichloroacetate) monohydrate are very similar as noticed for the molecule described above. Of course the absolute values are different, but directional properties of β hyperpolarizability seem to be very close to each other. The hyperpolarizability is dominated by the longitudinal component β_{xxx}, whereas the medium values of β are noticed for YXY, XXZ, ZXX and ZXZ directions. Additionally, the medium values of β are observed for four directions: XYY, ZYZ, XZZ and YZZ. It is characteristic that all values of longitudinal components calculated for this molecule have at least medium values. The components close to 0 are practically not observed in this case.

This similarity in calculated directional properties of β strongly suggests, that NLO properties of these two compounds may be determined by structural motif common for both compounds (in our investigation – melaminium cation).

3.3 Third harmonic generation

The average values of second hyperpolarizability γ cover the wide range of 430.63×10^{-36} – 320424.26×10^{-36} [esu]. The highest values of γ were calculated for melaminium tartrate monohydrate molecule. The much lower data are noticed for the remaining melaminium compounds. The second order hyperpolarizability γ is equal to -6909.66×10^{-36} [esu] in the case of bis(melaminium) sulphate dihydrate molecule, whereas for other considered compounds these theoretical data are less than 3000×10^{-36} [esu]. It is interesting that the values of γ seem to be independent on the value of

Table 3. The calculated hyperpolarizability β (unit of β is 10^{-30} esu) and its directional properties for investigated molecules.

SHG	Bismelaminium sulphate dihydrate	Melaminium tartrate monohydrate	Melaminium phthalate	Melaminium acetate acitic acid solvate monohydrate
β_{XXX}	3.68	-52.07	0.86	2.21
β_{YXX}	9.10	2.34	7.58	-7.93
β_{ZXX}	7.68	10.74	-0.46	-0.89
β_{XXY}	10.87	8.10	7.50	-8.31
β_{YXY}	0.96	-13.95	-1.45	-0.01
β_{ZXY}	-0.44	9.28	-3.75	-0.73
β_{XXZ}	8.24	13.63	-0.32	-0.83
β_{YXZ}	-0.36	-1.07	-3.84	-0.80
β_{ZXZ}	0.65	-15.78	-0.01	-0.37
β_{XYY}	0.85	-3.51	-2.24	0.24
β_{YYY}	2.90	5.51	-11.69	9.63
β_{ZYY}	1.71	0.60	2.10	-0.01
β_{XYZ}	-0.39	-3.94	-3.74	-0.77
β_{YYZ}	1.86	0.17	1.77	-0.05
β_{ZYZ}	1.15	1.75	2.07	-0.16
β_{XZZ}	0.71	-1.13	0.02	-0.36
β_{YZZ}	1.18	0.41	2.16	-0.15
β_{ZZZ}	0.69	-0.70	1.23	-0.14
SHG	**Melaminium bis(selenate) trihydrate**	**Melaminium diperchlorate monohydrate**	**Melaminium bis(trichloroacetate) monohydrate**	**Melaminium bis(4-hydroxybenzenesulphonatre) dihydrate)**
β_{XXX}	7.10	8.12	15.55	-5.53
β_{YXX}	-7.93	-2.29	-5.22	2.73
β_{ZXX}	6.66	0.18	-10.28	-1.33
β_{XXY}	-3.48	-1.88	-3.75	-3.15
β_{YXY}	-6.12	-7.84	6.44	1.08
β_{ZXY}	-5.62	2.35	-3.55	1.08
β_{XXZ}	2.17	0.31	-11.10	-2.04
β_{YXZ}	2.35	2.28	4.30	0.53
β_{ZXZ}	0.36	-0.27	5.55	-4.86
β_{XYY}	-10.43	-8.55	5.74	0.98
β_{YYY}	0.95	2.61	4.01	-0.34
β_{ZYY}	-2.39	-1.55	3.21	3.53
β_{XYZ}	-2.74	2.63	-5.11	0.64

Continued **Table 3.** The calculated hyperpolarizability β (unit of β is 10^{-30} esu) and its directional properties for investigated molecules.

SHG	Melaminium bis(selenate) trihydrate	Melaminium diperchlorate monohydrate	Melaminium bis(trichloroacetate) monohydrate	Melaminium bis(4-hydroxybenzenesulphonatre) dihydrate)
β_{XZZ}	0.36	-1.41	3.21	2.81
β_{YZZ}	-4.36	0.82	6.49	-6.13
β_{ZZZ}	-2.13	-0.34	7.17	-5.23

Table 4. The calculated second hyperpolarizability γ (unit of γ is 10^{-36} esu) and its directional properties for investigated molecules.

Third harmonic generation	Bis (melaminium) sulphate dihydrate	Melaminium tartrate monohydrate	Melaminium phthalate	Melaminium acetate acetic acid solvate monohydrate	Melaminium bis (selenate) trihydrate	Melaminium diperchlorate monohydrate	Melaminium bis (trichloroacetate) monohydrate	Melaminium bis (4-hydroxybenzene sulphonate) dihydrate)
γ_{XXXX}	-20683.61	-1654779.72	467.12	606.71	1190.56	-725.58	2390.91	-2479.97
γ_{YYYY}	177.61	-57.56	727.70	259.73	-829.47	440.79	1388.27	842.49
γ_{ZZZZ}	65.24	664.24	441.89	7.04	851.25	316.52	1220.17	236.91
γ_{XXYY}	2623.31	-15850.11	257.61	516.48	46.01	134.56	615.52	-1257.23
γ_{XXZZ}	-1558.14	23889.34	3.18	151.38	1025.38	54.91	1588.99	-153.34
γ_{YYXX}	-9794.09	19318.33	142.59	351.06	-284.18	-150.97	1709.02	375.53
γ_{YYZZ}	-287.25	155.96	174.50	151.94	492.95	263.89	-123.55	-54.65
γ_{ZZXX}	64.52	24268.57	87.60	66.74	594.44	-216.08	757.63	-391.29
γ_{ZZYY}	90.74	269.63	83.48	42.06	372.66	73.65	545.50	-202.23
$\gamma_{average}$	-6909.66	-320424.26	477.13	430.63	691.92	38.34	2018.49	-616.75

calculated dipole moment, but for melaminium tartrate monohydrate the highest dipole moment corresponds to the highest γ hyperpolarizability.

Similarly to the first hyperpolarizability β, the second hyperpolarizability γ is dominated by γ_{xxxx} component for all investigated molecules. Dominance of this component indicates a substantial charge delocalization in this direction.

The components of second hyperpolarizability γ in all the other directions are very small. A noticeable values are obtained in the case of melaminium tartrate monohydrate molecule. For this compound the XXYY, XXZZ, YYXX and ZZXX components are in the range of -15850.11×10^{-36} – 24268.57×10^{-36} [esu]. The value bigger than 9000×10^{-36} [esu] was also noticed for YYXX direction in the case of bis(melaminium) sulphate dihydrate. Calculated data for all remaining investigated compounds are smaller than 3000×10^{-36} [esu].

It should be emphasized that the values of second hyperpolarizabilty γ are relatively small when compared to p-nitroaniline standard. On the basis of theoretical approach these investigated compounds could not be used in the third harmonic generation (THG) applications.

However, the time-dependent Hartree-Fock calculations strongly depend on calculation method and should be compared with experimental values. These differences between calculated and experimental results are pronounced.

3.4 EFISH effect

Electric field induced second harmonic generation (EFISH) is a well-known technique [30] for measuring the first hyperpolarizability (β) of organic molecules [31-35] in solution. Since the EFISH experiment deals with liquid samples, it is clear that the theoretical calculation of EFISH (-2ω; ω, ω, 0) effect should be more adequate for single molecules investigated in our studies. Unfortunately, the experimental results of EFISH method are not known for the compounds studied in this

Table 5. Calculated values of γ(EFISH) for all investigated molecules (unit of γ is 10^{-30} esu).

EFISH	Bismelaminium sulphate dihydrate	Melaminium tartrate monohydrate	Melaminium phthalate	Melaminium acetate acitic acid solvate monohydrate	Melaminium bis (selenate) trihydrate	Melaminium diperchlorate monohydrate	Melaminium bis (trichloroacetate) monohydrate	Melaminium bis (4-hydroxybenzen-esulphonatre) dihydrate)
γ_{XXXX}	5595.98	-205731.71	158.97	490.39	134.01	192.00	2715.03	1632.89
γ_{YYYY}	203.47	-349.37	285.50	124.37	174.15	129.33	164.47	487.36
γ_{ZZZZ}	66.91	-25.21	136.69	4.13	-21.38	70.74	1835.76	18.93
γ_{XYXY}	639.78	1671.01	135.67	223.72	-49.10	125.24	209.63	570.32
γ_{XZXZ}	534.39	-17078.09	36.21	56.39	-18.05	59.73	2146.40	84.20
γ_{YXYX}	588.94	-160247.16	130.82	216.00	-324.02	86.20	315.49	545.50
γ_{YZYZ}	107.39	-2963.62	57.80	40.54	-143.39	65.49	-39.16	50.27
γ_{ZXZX}	501.96	-11527.91	37.85	45.85	-382.25	8.80	1548.99	72.61
γ_{ZYZY}	89.81	97.57	49.40	30.56	-288.70	45.75	45.93	51.59
γ_{XXYY}	452.17	154.54	57.49	145.79	801.02	-1.39	-330.80	526.74
γ_{XXZZ}	493.40	-14799.86	16.20	43.97	1003.60	-14.54	2429.38	38.14
γ_{YYXX}	424.09	-11406.11	59.51	142.04	609.20	-12.39	172.24	511.29
γ_{YYZZ}	87.46	471.68	26.42	30.01	652.90	6.93	-149.95	-0.36
γ_{ZZXX}	466.58	-1203.61	16.70	39.14	247.21	-43.50	1863.10	31.32
γ_{ZZYY}	77.75	2.95	22.55	25.39	347.48	2.85	-457.77	-0.56
$\gamma_{average}$	1635.01	-68346.38	189.19	233.94	140.71	126.44	1741.77	684.88

paper. Published in this work theoretical EFISH data can be used only for comparison of β hyperpolarizability calculations.

As was shown in Table 5, the calculations give results close to 0 for four compounds: melaminium phthalate, melaminium acetate acetic acid solvate monohydrate, melaminium bis(selenate) trihydrate and melaminium diperchlorate monohydrate. The very small EFISH value noticed for melaminium bis(selenate) trihydrate clearly indicate that the second order NLO response in the case of this compound is connected with the hydrogen bond network, because this type of interaction is not considered in our calculation of EFISH.

The highest average value of calculated EFISH coefficient was noticed for melaminium tartrate monohydrate. It is equal to -68346.38×10^{-30} [esu]. Similarly, to the first hyperpolarizability, β, the γ (EFISH) is dominated by its long component γ_{xxxx}, but the big value of component in direction YXYX is also observed.

Much smaller data are obtained for the second crystal (melaminium bis(trichloroacetate) monohydrate), where the hyperpolarizability, β was observed. The calculated value is equal to 1741.77×10^{-30} [esu] and in this case the main participation of two component XXXX and XZXZ is noticed.

Surprisingly, contrary to the experimental data of hyperpolarizability β, the higher average of γ(EFISH) is observed for bis(melaminium) sulphate dihydrate compound (1635.01×10^{-30} [esu]).

For the high values and similar directional properties of melaminium tartrate monohydrate and melaminium bis(trichloroacetate) monohydrate, the strong deformation of electron cloud in melaminium cations and smaller hydrogen bonds participation in generation of hyperpolarizability, β, are responsible.

4. Conclusions

1. In the first approximation, the calculated value can be reliably used as parameter for preliminary selection of

newly obtained compounds with NLO properties. This way seems to be fast and inexpensive, especially when experimental data remain still unavailable.

2. The theoretical study of β hyperpolarizability seems to be a unique method for full characterization of directional properties of second order NLO response. For two compounds the hyperpolarizability β can be associated with deformation of electron cloud in common structural motif (melaminium cation). Such investigations are efficient way for designing of new materials with improved NLO properties.

3. The obtained values of hyperpolarizability β seem to be underestimated in comparison with experimental data. It suggests that the intermolecular interactions (in particular hydrogen bonds) are not to be neglected in generation of hyperpolarizability β in the studied compounds.

Supplementary materials

The obtained results of calculated equilibrium structures with selected bonds length of and angles values were collected in supplementary materials for this paper.

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