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Journal of Molecular Structure 650 (2003) 1–20

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# X-ray crystal structures, molecular mechanics and quantum chemical calculations, and calculations of the nonlinear optical polarizabilities in the series of monohalogen substituted derivatives of dicyanovinylbenzene

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Received 24 July 2002; accepted 12 September 2002

# Abstract

The molecular and crystal structure of a series of potential non-linear optical (NLO) compounds — o-, m- and p-halogensubstituted derivatives of dicyanovinylbenzene, has been studied. The molecular geometry was investigated with an X-ray diffraction analysis and discussed along with results of the molecular mechanics (MM3) and ab initio quantum calculations (MP2 and DFT). The influence of the crystal packing on the molecular planarity has been revealed. Calculations of the dipole moments and molecular hyperpolarizabilities for molecules in question were carried out in the finite field approach. In addition to a several acentric compounds of this series found before, in the present investigation one more acentric crystal of the p-I substituted dicyanovinylbenzene was found (space group Pna2<sub>1</sub>, Z = 4). Second harmonic generation (SHG) of the laser light for this compound was confirmed by the Kurtz powder test.

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Keywords: Non-linear optical properties; Derivatives of dicyanovinylbenzene; X-Ray analysis; Molecular mechanics; Quantum chemical calculations

# 1. Introduction

Organic chromophore compounds with non-linear optical (NLO) properties have been under intensive investigation during last years because of their potential applicability in image processing and optical communications. The main reason for this is that in many respects these compounds might be more efficient materials (for second harmonic generation (SHG), frequency mixing, electrooptical modulation, photorefractive and optical limiting applications, etc.) than the well-known inorganic compounds like KDP, BaTiO<sub>3</sub>, LiNbO<sub>3</sub>. In many cases the efficiency of organic NLO materials is at least one or more order of magnitude above that of the best inorganic ones due to ultrafast response times and low dielectric constants. An additional

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advantage of organic NLO compounds is high optical damage thresholds and straightforward methods of preparation and fabrication, especially preparation of the thin crystalline films.

It is well recognized today that NLO-active organic molecules must have a polar and highly conjugated  $\pi$ -electron system terminated with electron donor and acceptor groups. Big progress has been achieved during last years to create new NLO-active compounds possessing very high values of the second-order polarizability ( $\beta$ ) using molecular design and crystal engineering methods. Progress in this field is summarized in a series of modern monographs [1–3] and recent original publications [4–10].

Many important and new structure/property relations for parent series of organic NLO compounds were established and described in literature as a result of systematical studies of simple model chromophore compounds (see, for example [4-10]). This allowed one to conduct a directional chemical synthesis and preparation of new compounds possessing necessary NLO characteristics. A big progress in this field is related to a prior quantum calculations of the molecular hyperpolarizabilities and to estimation (and/or measurements) of their optical properties and NLO crystalline responses. Single crystal X-ray data provide in many respects necessary information for understanding NLO structure/properties relations and for design of new NLO active materials.

However, not all features in design of organic NLO-active materials and crystals are completely understood at present. In particular, it is known that only non-centrosymmetric compounds may exhibit NLO effects (for example, second harmonic generation,) in the solid state [11,12], but a prior prediction of the centric/acentric crystal structure of a new organic compound is still a problem of the modern computational and structural chemistry [13, 14]. Therefore, further search for new structure/ property relations in series of model compounds and their systematical X-ray structural analysis are important fields of research directed to understanding of the 'rules' governing formation of the crystals of a given symmetry.

In the present study we carried out synthesis, X-ray structural analysis, quantum chemical and

molecular mechanics calculations of the series of monohalogen-substituted derivatives of dicyanovinylbenzene (1). We considered series of twelve monosubstituted dicianovinylbenzenes (2-13) with the F, Cl, Br, and I substituents in the *ortho-*, *meta*and *para*-positions, respectively (see Scheme below).



Substituent	Substituent Position					
	Ortho	Meta	Para			
Н	1	_	_			
F	2	6	10			
Cl	3	7	11			
Br	4	8	12			
Ι	5	9	13			

Five new compounds of this series (4-6, 10 and 12) were first synthesized and investigated in details by methods mentioned above. These data are compared with results of our previous structural investigations of the compounds 1 [6], 2, 3 [8], and compound 11 which was described earlier by other authors [15,16].

Results of the quantum calculations of the molecules 1-13 in the isolated state and molecular hyperpolarizabilities ( $\beta$ ) are also presented and compared. Crystals of compounds 2, 5 and 11 are acentric. Therefore they manifest second harmonic (SH) of the laser light. In the present study we measured UV spectra and powder second harmonic generation activity for the compound 5 (space group Pna2<sub>1</sub>), and compared these data with results for other acentric compounds in this series, namely 2 (space group Pc) and 11 (space group P2<sub>1</sub>) described before [8,15].

#### 2. Experimental part and computational details

#### 2.1. Materials

Synthesis of the 2-(2-bromophenyl)-1,1-dicyanovinyl (4), 2-(2-iodophenyl)-1,1-dicyanovinyl (5), 2-(3-fluorophenyl)-1,1-dicyanovinyl (6), 2-(4-fluorophenyl)-1,1-dicyanovinyl (10), and 2-(4-bromophenyl)-1,1-dicyanovinyl (12) was carried out using the Knoevenagel reaction from the malononitrile and corresponding F-, Br- or I-substituted benzaldehydes. The same synthetic procedure we used before for the compounds 2 and 3 [8]. All materials were recrystallized from the ethanol and showed no impurities by the GC-MS before use. Compounds were obtained with the yields 71-79% and characterized with the H<sup>1</sup> and C<sup>13</sup> NMR and UV-visible spectra.

### 2.2. X-Ray diffraction analysis

Single crystals of 4-6, 10, and 12 for X-ray analysis were grown by slow evaporation from the ethanol solutions. Details of the data collection and structure refinement are given in Table 1. Absorption correction (SADABS program) was applied for compounds 4 and 5.

The structures were solved by direct methods and refined by a full-matrix least squares in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were localized on difference Fourier maps. Hydrogen atoms for structures **5**, **10** and **12** were refined with the 'riding' model, while for structures **4** and **6** they were refined isotropically. All calculations were performed using the SHELXTL program [17], Ver. 5.10 DOS/WIN95/NT. Bond lengths, bond angles, and important torsion angles are summarized in Tables 2–4 along with corresponding available data for the compounds **1–3** [6,8] and **11** [15], and with data obtained by quantum calculations. The general view of molecules studied with the atomic numbering schemes is presented in Figs. 1 and 2.

# 2.3. Molecular mechanics and quantum chemical calculations of the molecular geometry, rotational barriers, and molecular hyperpolarizability

All molecular geometries of the isolated molecules 1-13 were calculated using the molecular

mechanics (MM) MM3 program [18,19] and quantum chemical approaches. Using the MM3 program we found optimal conformation of 1-13, and barriers of internal rotation of the dicyanovinyl group around the single C(1)-C(7) bond (see Figs. 3-5). These data were compared with two sets of ab initio calculations of molecules 1-13. We fully optimized molecular geometries with the density functional method and using Moeller-Plesset approximation. Molecules with the F. Cl and Br substituents were optimized at the MP2/6-31G\*\* and B3LYP/6-31G\*\* levels of theory, and molecules with the iodine substituents were optimized at the MP2/3-21G\*\* and B3LYP/3-21G\*\* levels, respectively. All calculations were carried out with the GAUSSIAN 94 programs [20]. For unsubstituted molecule 1 the barrier of internal rotation around the C(1)-C(7) bond was evaluated using the MP2 approximation.

Results of the quantum calculations (MP2) and Xray data were used further for calculations of the molecular dipole moments  $\mu$  and molecular hyperpolarizabilities  $\beta$  and  $\gamma$  in the finite field approach. For calculations we used modified MOPAC program, AM1 approximation [21,22], and HYPER program [23].

### 2.4. Second harmonic measurements

Since crystals of 5 are acentric, the Kurtz technique [24] was applied to measure nonlinear optical response for this compound in the powder sample. Green SH (532 nm) signals were measured with 1 Hz Q-switched Nd:YAG laser (1064 nm, 10 mJ per 7 ns pulse). In order to collect more effectively the SH light generated and scattered in the sample, the ellipsoid mirror was set up with the sample in the primary focus, and the detector (Hamamatsu HC-120 photomultiplier assembly) in the secondary focus. The SH signals were averaged by a digital storage scope to suppress noise. The sample was loaded into a 250 µm thickness plastic cell between two glass plates. The  $P(2\omega) \propto P^2(\omega)$ harmonic square dependence was second obtained for the compound 5 and for the reference compound (urea).

According to the Kurtz method [24], the phasematchable materials give SH intensity, independent of, or increasing with, particles size, whereas SH

 Table 1

 Crystal determination summary for compounds 4–6, 10 and 12

Molecule	4	5	6	10	12
Empirical formula	$C_{10}H_5BrN_2$	$C_{10}H_5IN_2$	$C_{10}H_5FN_2$	$C_{10}H_5FN_2$	$C_{10}H_5BrN_2$
Formula weight	233.07	280.06	172.16	172.16	233.07
Temperature (K)	110(2)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Z	4	4	4	2	2
Space group	$P2_1/c$	$Pna2_1$	$P2_1/c$	P-1	P-1
Unit cell dimensions					
a (Å)	3.8747(8)	7.8096(16)	3.8678(15)	6.9617(16)	6.6019(13)
$b(\mathbf{A})$	21.379(4)	17.109(3)	20.036(9)	7.366(2)	7.7472(15)
c (Å)	11.061(2)	7.2817(15)	11.046(5)	9.151(3)	9.2558(19)
$\alpha$ (deg)	90	90	90	107.19(2)	103.99(3)
$\beta$ (deg)	95.50(3)	90	95.27(3)	99.01(2)	97.58(3)
$\gamma$ (deg)	90	90	90	102.85(2)	92.17(3)
Volume (Å <sup>3</sup> )	912.1	972.9(3)	852.4(6)	424.4(2)	454.15(16)
Density (calculated)	1.697	1.912	1.342	1.347	1.704
$(Mg/m^3)$					
Diffractometer	Smart CCD	Smart CCD	Siemens P3/PC	Siemens P3/PC	Siemens P3/PC
Absorption coefficient	4.455	3.243	0.098	0.098	4.473
$(mm^{-1})$					
F(000)	456	528	352	176	228
$\theta$ range for data collection	1.9-30.0	2.4-30.1	2.8-26.0	2.4-29.1	2.3-26.1
(deg)					
Data/restraints/	2639/0/118	2844/1/118	1640/0/138	2267/0/118	1722/0/118
parameters					
Goodness-of-fit on $F^2$	0.876	0.995	0.998	1.021	1.046
Reflections collected	7378	11,092	1888	2443	1885
Independent reflections	2639	2844	1640	2267	1722
	[R(int) = 0.0288]	[R(int) = 0.0405]	[R(int) = 0.0362]	[R(int) = 0.0239]	[R(int) = 0.0249]
Final R indices	$R_1 = 0.0302,$	$R_1 = 0.0398,$	$R_1 = 0.0532,$	$R_1 = 0.0675,$	$R_1 = 0.0429,$
[with $I > 2\sigma(I)$ ]	$wR_2 = 0.0560$	$wR_2 = 0.1085$	$wR_2 = 0.1058$	$wR_2 = 0.1066$	$wR_2 = 0.1050$
<i>R</i> indices (all data)	$R_1 = 0.0595,$	$R_1 = 0.0494,$	$R_1 = 0.1532,$	$R_1 = 0.1847,$	$R_1 = 0.0621,$
	$wR_2 = 0.0628$	$wR_2 = 0.1139$	$wR_2 = 0.1284$	$wR_2 = 0.1323$	$wR_2 = 0.1129$
Largest diff. peak	0.864	1.886	0.144	0.126	0.462
$(e \tilde{A}^{-3})$					
Largest diff. hole	-0.446	-0.574	-0.152	-0.252	-0.874
$(e \tilde{A}^{-3})$					

from non-phase-matchable materials first increases, reaching a maximum for particle size comparable to the coherence length, then decreases. Due to small amount of the sample **5** the test was carried out using only available powder (with particle size 90–180  $\mu$ m). In this region the phase-matchable materials attain their maximum SH intensity independent of particle size, and non-phase-matchable materials still varying inversely with the particle size but very close to zero. Considerable intensity of the SH signal was detected for the compound 5 (five

times greater then that for urea with the same particle size), that assumes the phase-matchability of the material studied.

Luminescence spectrum was measured for compound 5. It showed no luminescent light that could interfere with the SH signal at 532 nm. Absorption spectra of solution (ethanol) and suspended powder (in glycerol) were measured. The absorption bands due to  $\pi \rightarrow \pi^*$  transitions appeared at the UV region of the spectrum ( $\lambda_{max}$  302 nm). No absorption was observed at the 1064 nm and at 532 nm regions.

Table 2 Bond length (Å), bond angles(°) and important torsion angles(°) in *ortho*-substituted molecules 1-5

Molecule	Method	1	2	3	4	5
Bond lengths						
Hal–C	X-ray	_	1.363(3)	1.736(2)	1.900(2)	2.106(5)
	MP2	_	1.358	1.740	1.906	2.157
	B3LYP	-	1.348	1.759	1.915	2.153
N(1)-C(9)	X-ray	1.140(3)	1.149(3)	1.139(2)	1.154(3)	1.151(8)
	MP2	1.184	1.184	1.184	1.184	1.191
	B3LYP	1.164	1.164	1.164	1.164	1.167
N(2)-C(10)	X-ray	1.149(3)	1.144(4)	1.141(2)	1.138(3)	1.139(9)
	MP2	1.184	1.184	1.184	1.184	1.191
	B3LYP	1.164	1.163	1.163	1.163	1.166
C(1) - C(6)	X-ray	1.401(3)	1.413(3)	1.403(2)	1.400(3)	1.408(9)
	MP2	1.407	1.408	1.407	1.408	1.416
	B3LYP	1.412	1.414	1.414	1.414	1.415
C(1) - C(2)	X-ray	1.395(3)	1.398(3)	1.407(2)	1 404(3)	1.399(8)
	MP2	1.408	1.403	1 408	1 408	1 415
	B3LYP	1 412	1 411	1 419	1 419	1 422
C(2) = C(3)	X-ray	1.382(4)	1.411 1.375(4)	1.382(2)	1 382(3)	1.374(8)
C(2) = C(3)	MP2	1.302(4)	1.375(4)	1.302(2)	1.382(3)	1.406
	B3I VD	1.300	1.386	1.307	1.304	1.400
C(3) $C(4)$	V rov	1.390	1.380(4)	1.392	1.391	1.395
C(3) = C(4)	A-1ay MD2	1.370(4)	1.309(4)	1.370(3)	1.382(3)	1.30(1)
	MP2 D2LVD	1.390	1.394	1.394	1.394	1.400
C(A) = C(5)	DOL I P	1.390	1.394	1.395	1.394	1.393
C(4) - C(5)	X-ray	1.375(4)	1.400(4)	1.381(3)	1.383(3)	1.34(1)
	MP2	1.397	1.398	1.397	1.397	1.407
	B3LYP	1.398	1.399	1.396	1.396	1.396
C(5) - C(6)	X-ray	1.375(4)	1.387(4)	1.377(2)	1.376(3)	1.36(1)
	MP2	1.393	1.392	1.391	1.391	1.403
	B3LYP	1.390	1.389	1.388	1.388	1.388
C(1) - C(7)	X-ray	1.450(3)	1.456(3)	1.450(2)	1.457(3)	1.453(8)
	MP2	1.457	1.456	1.459	1.460	1.480
	B3LYP	1.453	1.450	1.453	1.453	1.455
C(7) - C(8)	X-ray	1.350(3)	1.356(3)	1.349(2)	1.352(3)	1.350(8)
	MP2	1.360	1.359	1.358	1.358	1.358
	B3LYP	1.367	1.366	1.366	1.366	1.363
C(8)-C(9)	X-ray	1.441(3)	1.437(3)	1.435(2)	1.431(3)	1.44(1)
	MP2	1.435	1.435	1.436	1.436	1.442
	B3LYP	1.432	1.432	1.432	1.432	1.424
C(8)-C(10)	X-ray	1.438(3)	1.448(3)	1.437(2)	1.448(3)	1.44(1)
	MP2	1.437	1.437	1.436	1.436	1.441
	B3LYP	1.435	1.435	1.436	1.436	1.429
Bond angles						
C(6) - C(1) - C(2)	X-ray	118.5(2)	116.5(2)	116.6(1)	117.2(2)	116.6(5)
	MP2	119.1	117.2	118.1	117.8	118.4
	B3LYP	118.4	116.6	116.7	116.7	117.2
C(6) - C(1) - C(7)	X-ray	124.8(2)	125.4(2)	124.1(1)	122.5(2)	122.9(5)
	MP2	123.9	125.1	121.7	121.6	120.6
	B3LYP	125.0	126.1	123.6	123.3	122.9
C(2)-C(1)-C(7)	X-ray	116.7(2)	118.1(2)	119.3(1)	120.3(2)	120.5(5)
	MP2	117.0	117.7	120.2	120.5	121.0
	B3LYP	116.6	117.3	119.7	120.0	119.9

(continued on next page)

Table 2 (continued)

Molecule	Method	1	2	3	4	5
C(3)-C(2)-C(1)	X-ray	120.8(2)	123.7(2)	121.5(4)	121.6(2)	121.5(6)
	MP2	120.6	123.1	121.1	121.5	121.1
	B3LYP	121.1	123.2	121.8	121.8	121.0
Hal-C(2)-C(1)	X-ray	_	118.4(2)	120.7(1)	120.6(2)	122.4(4)
	MP2	-	118.4	120.4	120.2	120.3
	B3LYP	-	118.7	121.4	121.9	122.9
Hal-C(2)-C(3)	X-ray	-	117.9(2)	117.8(1)	117.8(2)	116.1(4)
	MP2	-	118.5	118.5	118.2	118.7
	B3LYP	-	118.1	116.8	116.4	116.1
C(2)-C(3)-C(4)	X-ray	119.6(2)	118.7(2)	119.9(2)	119.6(2)	118.9(6)
	MP2	120.0	118.6	119.7	119.5	119.7
	B3LYP	119.8	118.6	119.8	119.8	120.2
C(3) - C(4) - C(5)	X-ray	120.5(2)	120.0(3)	120.2(2)	120.0(2)	121.3(7)
	MP2	119.8	120.1	120.1	120.1	120.1
	B3LYP	119.9	120.2	120.0	119.9	119.9
C(4) - C(5) - C(6)	X-ray	120.6(2)	120.3(2)	119.9(2)	120.3(2)	120.4(7)
	MP2	120.7	120.5	120.0	120.1	120.0
	B3LYP	120.6	120.4	120.1	120.0	120.1
C(5)-C(6)-C(1)	X-ray	120.1(2)	120.8(2)	121.8(2)	121.3(2)	121.2(6)
	MP2	119.9	120.6	120.9	120.9	120.8
	B3LYP	120.2	121.0	121.7	121.8	121.6
C(8) - C(7) - C(1)	X-ray	130.9(2)	129.6(2)	129.6(1)	126.9(2)	130.0(6)
	MP2	128.9	127.9	126.0	125.8	124.2
	B3LYP	131.6	130.8	131.2	131.3	131.1
C(7) - C(8) - C(9)	X-ray	126.3(2)	127.0(2)	125.7(1)	124.5(2)	126.9(8)
	MP2	124.7	124.6	123.9	123.8	122.9
	B3LYP	125.4	125.5	126.2	126.3	126.0
C(7) - C(8) - C(10)	X-ray	119.0(2)	119.1(2)	120.1(1)	120.6(2)	118.1(6)
	MP2	119.7	119.7	120.1	120.1	120.8
	B3LYP	119.2	119.2	118.9	118.8	118.9
C(9) = C(8) = C(10)	A-ray	114.0(2)	115.9(2)	114.2(1)	114.8(2)	115.0(5)
	MP2 D2LVD	115.0	115.0	115.9	116.0	110.3
N(1) = C(0) = C(0)	DOL IP V mov	113.4	113.5	114.9	114.9	113.1
N(1) - C(9) - C(8)	A-ray	170.7(2)	177.6(5)	170.4(2)	177.4(2)	170.9(0)
	D2LVD	178.4	1/0./	178.5	178.5	170.3
N(2) = C(10) = C(2)	DJL1F V rov	170.4(2)	179.1	170.0(2)	173.0	179.2
N(2) = C(10) = C(8)	MP2	179.4(2)	170.9(3)	179.0(2)	177.9(2)	179.4(8)
	B3I VP	179.0	180.0	180.0	180.0	179.3
	DJEII	179.7	100.0	100.0	100.0	177.7
Torsion angles						
C(6)-C(1)-C(7)-C(8)	X-ray	9.7(3)	5.4(2)	11.8(1)	-30.9(3)	-22(1)
	MP2	23.1	24.1	37.5	38.4	49.8
	B3LYP	0.0	0.0	3.2	0.0	0.0
C(2)-C(1)-C(7)-C(8)	X-ray	171.1(2)	174.9(2)	169.1(1)	152.7(2)	159.7(6)
	MP2	157.9	158.1	145.1	144.4	131.9
	B3LYP	180	180	177.2	180	180.0
C(1)-C(7)-C(8)-C(9)	X-ray	1.1(3)	2.7(2)	0.8(1)	-6.8(3)	-4(1)
	MP2	0.8	1.7	3.3	3.2	2.8
	B3LYP	0.0	0.0	0.4	0.0	0.0
C(1)-C(7)-C(8)-C(10)	X-ray	179.0(3)	179.0(2)	178.9(1)	175.3(2)	178.9(6)
	MP2	179.9	179.2	178.1	178.2	177.9
	B3LYP	180.0	180.0	179.8	180.0	180.0

M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1–2	0
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Table 3 Bond length (Å), bond angles(°) and important torsion angles(°) in *meta*-substituted molecules 6-9

Molecule	Method	6	7	8	9
Bond lengths					
Hal-C	X-ray	1.359(3)	-	-	_
	MP2	1.353	1.736	1.901	2.153
	B3LYP	1.346	1.754	1.907	2.140
N(1)-C(9)	X-ray	1.137(3)	-	-	-
	MP2	1.185	1.184	1.184	1.191
	B3LYP	1.164	1.164	1.164	1.167
N(2)-C(10)	X-ray	1.143(3)	-	-	-
	MP2	1.184	1.184	1.184	1.190
	B3LYP	1.163	1.163	1.163	1.166
C(1)-C(6)	X-ray	1.396(3)	-	-	-
	MP2	1.407	1.406	1.407	1.415
	B3LYP	1.412	1.411	1.411	1.411
C(1)-C(2)	X-ray	1.397(3)	-	-	-
	MP2	1.407	1.406	1.407	1.417
	B3LYP	1.411	1.411	1.411	1.414
C(2)-C(3)	X-ray	1.361(3)	-	-	-
	MP2	1.387	1.391	1.391	1.403
	B3LYP	1.385	1.389	1.389	1.391
C(3)-C(4)	X-ray	1.363(4)	-	-	-
	MP2	1.391	1.396	1.395	1.407
	B3LYP	1.391	1.395	1.394	1.398
C(4)-C(5)	X-ray	1.369(3)	-	-	-
	MP2	1.396	1.396	1.396	1.407
	B3LYP	1.397	1.397	1.397	1.398
C(5)-C(6)	X-ray	1.378(3)	-	-	-
	MP2	1.393	1.393	1.393	1.404
	B3LYP	1.391	1.390	1.390	1.391
C(1)-C(7)	X-ray	1.446(3)	-	-	-
	MP2	1.458	1.459	1.459	1.478
	B3LYP	1.455	1.455	1.455	1.458
C(7)-C(8)	X-ray	1.345(3)	-	-	-
	MP2	1.360	1.360	1.360	1.360
	B3LYP	1.366	1.366	1.365	1.363
C(8)-C(9)	X-ray	1.433(3)	-	-	-
	MP2	1.435	1.435	1.435	1.440
	B3LYP	1.432	1.432	1.432	1.424
C(8)-C(10)	X-ray	1.441(3)	_	-	_
	MP2	1.437	1.437	1.437	1.442
	B3LYP	1.435	1.435	1.435	1.428
Bond angles					
C(6)-C(1)-C(2)	X-ray	118.3(2)	-	-	-
	MP2	119.4	119.5	119.4	119.4
	B3LYP	118.8	118.8	118.7	118.6
C(6) - C(1) - C(7)	X-ray	124.9(2)	-	-	_
	MP2	123.8	123.9	123.9	123.3
	B3LYP	125.0	125.1	125.1	125.2
C(2)-C(1)-C(7)	X-ray	116.9(2)	-	-	-
	MP2	116.8	116.6	116.6	117.3
	B3LYP	116.2	116.1	116.2	116.2

(continued on next page)

M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1–20

Table 3 (continued)

Molecule	Method	6	7	8	9
C(3)-C(2)-C(1)	X-ray	119.0(2)	_	_	_
	MP2	119.1	119.8	119.6	119.8
	B3LYP	119.7	120.3	120.3	120.7
Hal-C(3)-C(2)	X-ray	118.3(2)	_	_	_
	MP2	118.7	119.4	119.2	119.3
	B3LYP	118.9	119.4	119.4	119.6
Hal - C(3) - C(4)	X-ray	118.5(2)	_	_	_
	MP2	119.0	119.7	119.5	119.7
	B3LYP	119.2	119.7	119.6	120.0
C(2)-C(3)-C(4)	X-ray	123.2(2)	_	_	-
	MP2	122.3	121.0	121.3	121.0
	B3LYP	122.0	120.9	121.0	120.4
C(3)-C(4)-C(5)	X-ray	118.3(3)	_	_	-
	MP2	118.2	118.9	118.7	118.9
	B3LYP	118.4	119.0	118.9	119.3
C(4) - C(5) - C(6)	X-ray	120.7(2)	_	_	-
	MP2	121.1	121.1	121.1	120.9
	B3LYP	121.1	121.1	121.1	121.0
C(5)-C(6)-C(1)	X-ray	120.5(2)	-	-	_
	MP2	119.9	119.6	119.8	119.9
	B3LYP	120.1	120.0	120.1	120.0
C(8) - C(7) - C(1)	X-ray	130.7(2)	-	-	_
	MP2	128.5	128.4	128.4	127.3
	B3LYP	131.4	131.3	131.3	130.8
C(7)-C(8)-C(9)	X-ray	126.6(2)	-	-	_
	MP2	124.6	124.6	124.6	124.0
	B3LYP	125.5	125.4	125.4	125.0
C(7) - C(8) - C(10)	X-ray	119.4(2)	-	-	-
	MP2	119.7	119.7	119.7	120.2
	B3LYP	119.2	119.2	119.2	119.4
C(9) - C(8) - C(10)	X-ray	114.0(2)	-	-	-
	MP2	115.7	115.7	115.7	115.8
	B3LYP	115.3	115.4	115.4	115.6
N(1)-C(9)-C(8)	X-ray	177.6(3)	-	-	-
	MP2	178.5	178.5	178.5	178.6
	B3LYP	178.8	178.8	178.9	179.5
N(2)-C(10)-C(8)	X-ray	179.4(3)	-	-	-
	MP2	179.6	179.6	179.6	179.8
	B3LYP	179.6	179.6	179.6	179.8
Torsion angles					
C(6) - C(1) - C(7) - C(8)	V-ray	-6A(A)			
e(0) - e(1) - e(0)	MP2	24.8	24.7	24.8	32.2
	B3I VP	0.0	0.0	0.0	0.0
C(2) = C(1) = C(7) = C(8)	V-ray	173 6(2)	0.0	0.0	0.0
e(2) - e(1) - e(3)	MP2	156.2	156 /	156.2	1/8.8
	B3I VP	180	180.0	180.0	140.0
C(1) - C(7) - C(8) - C(9)	V-ray	-1.2(4)	100.0		100.0
e(1) e(1) e(0) e(0)	MP2	0.0	0.0	0.8	0.7
	B3LYP	0.0	0.0	0.0	0.0
C(1) = C(7) = C(8) = C(10)	X-ray	179 5(2)		- 0.0	- 0.0
	MP2	179.9	179.9	179.9	- 180.0
	R3I VP	180.0	180.0	180.0	180.0
	0.0011	100.0	100.0	100.0	100.0

M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1–2

Table 4 Bond length (Å), bond angles(°) and important torsion angles(°) in *para*-substituted molecules **10–13** 

Molecule	Method	10	11	12	13
Bond lengths					
Hal-C	X-ray	1.356(2)	1.718	1.889(4)	_
	MP2	1.352	1.734	1.899	2.150
	B3LYP	1.341	1.748	1.901	2.135
N(1)-C(9)	X-ray	1.130(3)	1.123	1.146(5)	_
	MP2	1.185	1.185	1.185	1.191
	B3LYP	1.164	1.164	1.164	1.167
N(2)-C(10)	X-ray	1.135(3)	1.112	1.135(5)	-
	MP2	1.184	1.184	1.184	1.191
	B3LYP	1.164	1.163	1.163	1.166
C(1)-C(6)	X-ray	1.397(3)	1.403	1.402(5)	_
	MP2	1.409	1.408	1.408	1.419
	B3lyp	1.414	1.412	1.412	1.412
C(1) - C(2)	X-ray	1.387(3)	1.387	1.384(6)	_
	MP2	1.408	1.408	1.408	1.420
	B3LYP	1.413	1.412	1.412	1.413
C(2) - C(3)	X-rav	1.378(3)	1.396	1.381(6)	_
	MP2	1.391	1.390	1.391	1.401
	B3LYP	1.388	1.388	1.389	1.390
C(3) - C(4)	X-rav	1.364(3)	1.370	1.382(6)	_
	MP2	1.390	1.396	1.396	1.407
	B3LYP	1.392	1.396	1.395	1.398
C(4) - C(5)	X-ray	1.359(3)	1.376	1.376(6)	_
	MP2	1.391	1.397	1.397	1.408
	B3LYP	1.394	1.398	1.397	1.400
C(5) - C(6)	X-ray	1.382(3)	1.396	1.381(5)	_
	MP2	1.391	1.390	1.391	1.402
	B3LYP	1.388	1.388	1.388	1.390
C(1) - C(7)	X-ray	1 454(3)	1 459	1 450(5)	_
	MP2	1.456	1.456	1 456	1.474
	B3LYP	1 451	1 452	1 452	1 455
C(7) - C(8)	X-ray	1.341(3)	1 333	1.344(6)	
0(1) 0(0)	MP2	1 361	1 361	1.361	1 363
	B3LYP	1.367	1.367	1.367	1.365
C(8) - C(9)	X-ray	1.307	1 439	1.425(6)	
$\mathcal{C}(0)$ $\mathcal{C}(0)$	MP2	1.437(3)	1.437	1.434	1 / 38
	R3LVP	1.437	1 432	1.432	1.430
C(8) = C(10)	X-ray	1.432	1.432	1.450(5)	
C(0) = C(10)	MP2	1.436	1.436	1.436	1 442
	B3LYP	1.434	1.435	1.435	1.428
Bond angles					
C(6) C(1) C(2)	V rov	118 6(2)	120	119 5(2)	
C(0) = C(1) = C(2)	A-ray MD2	118.0(2)	120	118.3(3)	- 119 /
	MF2 D2LVD	118.9	118.7	110.7	110.4
C(t) $C(1)$ $C(7)$	DJL IP V	116.2	116.1	110.1	116.1
U(0) - U(1) - U(1)	A-ray	124.4(2)	124	124.2(4)	-
	MP2	124.3	124.4	124.3	125.1
Q(2) Q(1) Q(7)	B3LYP	125.1	125.2	125.1	125.1
U(2) = U(1) = U(7)	X-ray	117.0(2)	117.0	117.2(3)	-
	MP2	116.9	117.0	116.9	116.5
	B3LYP	116.7	116.8	116.8	116.9

9

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M.Yu. Antipin	et al. / Jo	urnal of Ma	olecular Stru	cture 650	(2003) 1–2	0

Table 4 (continued)

Molecule	Method	10	11	12	13
C(3)-C(2)-C(1)	X-ray	121.4(2)	121	121.7(3)	_
	MP2	121.1	121.2	121.2	121.3
	B3LYP	121.6	121.6	121.6	121.5
Hal - C(4) - C(3)	X-ray	118.2(2)	119	119.1(3)	_
	MP2	119.0	119.7	119.5	119.8
	B3LYP	119.0	119.5	119.5	119.9
Hal-C(4)-C(5)	X-ray	118.4(2)	119	119.3(3)	_
	MP2	118.9	119.6	119.5	119.8
	B3LYP	118.9	119.5	119.4	119.8
C(2)-C(3)-C(4)	X-ray	117.8(2)	118	118.4(4)	-
	MP2	118.4	119.2	119.0	119.3
	B3LYP	118.3	118.9	118.9	119.4
C(3)-C(4)-C(5)	X-ray	123.3(2)	122	121.6(3)	-
	MP2	122.1	120.7	121.0	120.4
	B3LYP	122.1	121.0	121.1	120.3
C(4) - C(5) - C(6)	X-ray	118.8(2)	120	119.5(4)	-
	MP2	119.1	119.9	119.7	120.1
	B3LYP	119.1	119.7	119.7	120.1
C(5)-C (6)-C(1)	X-ray	120.1(2)	119	120.3(4)	-
	MP2	120.4	120.4	120.4	120.5
	B3LYP	120.7	120.7	120.7	120.7
C(8) - C(7) - C(1)	X-ray	131.6(2)	131	131.1(3)	-
	MP2	129.3	129.3	129.2	130.3
	B3LYP	131.6	131.5	131.4	130.8
C(7)-C(8)-C(9)	X-ray	125.5(2)	125	125.5(3)	-
	MP2	124.7	124.8	124.8	124.9
	B3LYP	125.2	125.3	125.3	125.0
C(7) - C(8) - C(10)	X-ray	119.8(2)	121	119.6(4)	-
	MP2	119.6	119.6	119.6	119.6
	B3LYP	119.2	119.2	119.2	119.4
C(9) - C(8) - C(10)	X-ray	114.8(2)	114	114.9(4)	—
	MP2	115.7	115.7	115.7	115.5
	B3LYP	115.5	115.5	115.5	115.6
N(1) - C(9) - C(8)	X-ray	178.1(2)	177	177.6(4)	-
	MP2	178.8	178.8	178.7	179.5
	B3LYP	179.0	179.0	179.6	
N(2)-C(10)-C(8)	X-ray	179.4(3)	177	178.5(5)	-
	MP2	179.6	179.6	179.6	180.0
	B3LYP	179.7	179.6	179.6	179.8
Torsion angles					
C(6) - C(1) - C(7) - C(8)	X-ray	-5.2(3)	1	3,3(7)	_
	MP2	19.7	19.3	19.7	0.0
	B3LYP	0.0	0.0	0.0	0.0
C(2) = C(1) = C(7) = C(8)	X-ray	175.6(2)	179	-178.9(4)	_
	MP2	161.4	161.7	161.3	180.0
	B3LYP	180	180	180.0	180.0
C(1)-C(7)-C(8)-C(9)	X-ray	-0.6(4)	5	1.3(7)	-
	MP2	0.6	0.6	0.6	0.0
	B3LYP	0.0	0.0	0.0	0.0
C(1)-C(7)-C(8)-C(10)	X-rav	179.3(2)	176	-178.1(4)	_
C(1) - C(7) - C(8) - C(10)	100	170.0	170.0	170.9	180.0
	MP2	1/9.9	1/9.9	1/9.0	100.0





Fig. 1. General view of molecules 4-6 with atomic numbering scheme.

# 3. Results and discussion

The presented series of the compounds is quite unique because it contains very similar structures differing only by nature and position of the halogen substituents (F, Cl, Br, and I) at the aromatic ring. For



Fig. 2. General view of molecules  $\mathbf{10}$  and  $\mathbf{12}$  with atomic numbering scheme.

nine of them crystal structures are determined, and all thirteen compounds are characterized by the MM and quantum calculations. This allows one to carry out a detailed comparison of the molecular geometry, crystal packing features and NLO properties in this representative series.

#### 3.1. Molecular geometry and crystal packing

Molecular geometry parameters obtained from the X-ray data for compounds 4-6 and 10, 12 at present work along with experimental results published before (molecules 1-3, and 11), and the results of *ab initio* calculations for the whole series 1-13 are presented in Tables 2-4 separately for the *ortho*, *meta* and *para*-substituted compounds, respectively. Corresponding bond lengths and bond angles for most of molecules are similar (except for Hal-C distances) and have expected values. Nevertheless, some geometrical features are worth to mention.

In particular, there is a small tendency in the C-C bond alternation in the aromatic rings: bond lengths

11



Fig. 3. Relative energy of molecule 1 vs torsion angle C(6)-C(1)-C(7)-C(8) (°).

C(2)-C(3) and C(5)-C(6) are somewhat shorter (by 0.01-0.02 Å) than those for the four other ring bonds. This may reflect some contribution of the quinoid structure to electronic structure of these molecules, but this trend is not very distinct in all investigated

cases. Earlier, the same trend was found to be more pronounced for some other substituted derivatives of dicyanovinylbenzene [6-8].

According to both experimental data and quantum calculations, slight elongation of the phenyl rings



Fig. 4. Energy of molecule **10**, **11**, **12** and **13** vs torsion angle C(6)-C(1)-C(7)-C(8) (°).



Fig. 5. Energy of molecule 2, 3, 4 and 5 vs torsion angle  $C(6)-C(1)-C(7)-C(8 (^{\circ}))$ .

bonds C(1)–C(2) and C(1)–C(6) attached to the acceptor dicyanovinyl substituent has been found (Tables 2–4). Halogen substituents in the ring do not influence geometry of dicyanovinyl fragment, namely the C(1)–C(7) and C(7)–C(8) bonds, see Tables 2–4. The values of these bonds vary in the rather narrow intervals (1.44–1.45 Å and 1.34–1.36 Å, respectively) according to both experimental and theoretical data, as for most other derivatives of the dicyanovinylbenzene studied before [6–8].

According to the X-ray data significant differences in the molecular geometry were found only for some bond and torsion angles. In particular, a decrease of the *ipso*-bond angles C(1)-C(2)-C(3) for the osubstituted 2-5 (in the sequence F-Cl-Br-I), and especially C(3)-C(4)-C(5) bond angles for the psubstituted molecules 10-12 (F, Cl, Br) reflects a gradual decrease of the electronegativity of the halogen substituents. This effect is well documented in literature [25]. For instance, for all F-substituted compounds studied (2, 6, and 10) corresponding ipsoangles are very close to the value of 123.4° - tabulated in [26] for F-substituted benzenes. Another significant difference was found for the Hal - C(2) - C(1) angles in molecules 2-5 which may result from steric demands of the *o*-halogen atoms: the larger is atomic volume of the substituent, the larger is corresponding bond

angle. This tendency withstands only in part, however, because in the Cl and Br derivatives corresponding angles are almost equal. In the latter case steric effects are partly compensated by the difference of the Cl–C and Br–C bond lengths. The same trend is reproduced by quantum calculations. Moreover, for the related bond angles C(2)-C(1)-C(7) in the series **1–5**, corresponding value for the *ortho*-I-derivative (**5**) is even smaller than that for *ortho*-Br derivative (**4**). We can explain this by the weak intramolecular electrostatic attractive interaction of the large and polarizable iodine atom with the positively charged H(7) atom that shrinks the C(2)-C(1)-C(7) bond angle.

As we may expect, the most varying values in the series of the compounds studied should be torsion angles, namely angles about the single C(1)-C(7) bond which result to molecular non-planarity. In particular, the *s*-*cis* torsion angles C(6)-C(1)-C(7)-C(8) vary in the interval from  $-1.0^{\circ}$  to  $-30.9^{\circ}$ , reaching the maximum values -30.9 and  $-22.4^{\circ}$  for the bulky *o*-Br and *o*-I substituents in the structures **4** and **5**, respectively (for all other molecules this angle is less than 12°). Nevertheless, there is no direct correlation between the nature of the *o*- and other substituents and molecular planarity degree: all *p*-substituted molecules **10–12**, as well as *m*-F (**6**) and

13

M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1-20

Table 5 Some important intramolecular short contacts in structures **4–6** and **10–12** 

Contact	1	2	3	4	5	6	10	11	12
H(6)C(9)	2.52	2.52	2.42	2.50	2.55	2.05	2.45	2.35	2.42
C(6)C(9)	3.11	3.10	3.04	3.03	3.11	3.09	3.08	3.02	3.05
C(2)-XH(7)	2.28	2.35	2.54	2.81	2.81	-	-	-	-

The sum of the van der Waals radii (Å) of the contacting atoms: H...C = 2.87; C...C = 3.54; H...H = 2.20; F...C = 2.56; Cl...C = 2.86; Br...C = 2.97; I...C = 3.13 [26].

o-F (2) are almost planar, while non-substituted molecule 1 in not planar and corresponding torsion angle (9.7°) is almost the same as in the *o*-Cl (3) molecule (11.8°). Similar tendency was observed for some other derivatives of dicyanovinylbenzene studied before [6–8]. These results may reflect both the influence of the intramolecular interactions and the influence of crystal packing on the molecular conformation.

The curves characterizing internal rotation of the dicyanovinyl group in the molecule **1** and obtained by *ab initio* (MP2) and MM calculations are compared in Fig. 3. The most pronounced dissimilarity of the MP2 and MM curves is located near the planar molecular conformation. If MM calculation gives energy difference  $\sim 0.8$  kcal/mol in favor of non-planar conformation, according to MP2 calculation this difference is negligibly small ( $\sim 0.1$  kcal/mol). Nevertheless, qualitative *ab initio* and MM results are in good agreement, therefore for other molecules **2–13** only MM calculations of the conformational energy versus the torsion angle C(2)–C(1)–C(7)–C(8) have been done (Figs. 4 and 5).

Both quantum and MM calculations allow one to conclude that for the *meta-* and *para-substituted* molecules there are no serious intramolecular restrictions on rotation of two planar molecular fragments (benzene ring and dicyanovinyl fragment) with respect to the C(1)-C(2) bond in the vicinity  $\pm 30^{\circ}$  of planar conformation. Corresponding potential curves are almost identical, therefore we present only data for the *para-substituted* molecules **10–13** (Fig. 4). It is most likely that in the crystals of **6–13** molecular conformation is defined by intermolecular interactions. For the *ortho-substituted* molecules **2–5** the halogen's influence on the molecular conformation is more pronounced (Fig. 5).

For all these molecules *anti*-orientation of the dicyanovinyl group to the halogen-substituent is optimal. This is in a agreement with experimental conformations of molecules 2-5 in crystals and results of the gas phase investigation of the 2-bromostyrene [27] where the torsion angle C(2)–C(1)–C(7)–C(8) was found to be  $155^{\circ}$  according to the gas electron diffraction data, and to  $138^{\circ}$  according to the *ab initio* calculations at the MP2/6-31G(d) level. For the *ortho*-substituted molecules the degree of non-planarity depends on sterical and electronic requirements of the halogen-substituent but it also may be influenced by the molecular packing in crystal.

Tables 5 and 6 summarize important intra- and intermolecular shortened contacts in the structures studied, in particular the H(6)...C(9), C(6)...C(9), and H(7)...Hal (at the C(2) atom) intramolecular contacts, and intermolecular contacts of the halogens and H(7)atoms. It is obvious that all these contacts are shorter than the sum of the van der Waals radii of corresponding atoms [28]. The halogen atoms form a small number of intermolecular shortened contacts. while the most important contacts are H(7)...N(1,2)ones which may be considered as week hydrogen bonds C-H...N. These H-bonds were found in all structures studied except for compound 5 where the ortho-iodine atom probably prevents from formation of such a bond. Due to formation of these weak Hbonds molecules in crystals form infinite chains (4, 6), centrosymmetric dimers (12), or both intermolecular associates (10). It was noted earlier [6] that 'shielding' of the acidic H(7) atom participating in the H-bond formation (due to a presence of o-substituent) may result in formation of the acentric crystal structure. Thus, crystal structures with o-F and o-I substituents (2 and 5) as well as with o-methoxy-group [6] are noncentrosymmetric and active in SHG in the solid state.

M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1-20

Table 6 Some important short intermolecular contacts and hydrogen bonds in structures **4**–**6**, **10**, and **12** 

Crystal	Contact atoms	Symm. code of primed atom	Contact distance (Å)	Angle C-HN (°)	Sum of the van der Waals radii (Å) [26]
4	Br(1)C(10)'	$x_{1} 0.5 - y_{2} z = 0.5$	3.58	_	3.64
	C(7)N(1)'	x - 1, 0.5 - y, z - 0.5	3.30	_	3.41
	H(7)N(1)'	x - 1, 0.5 - y, z - 0.5	2.40	160	2.74
5	I(1)N(1)'	1.5 - x, 0.5 + y, z - 0.5	3.34	_	3.67
6	C(9)C(10)'	-1 + x, y, z	3.38	_	3.54
	C(7)N(1)'	1 + x, 0.5 - y, 0.5 + z	3.30	_	3.41
	H(7)N(1)'	1 + x, 0.5 - y, 0.5 + z	2.57	162	2.74
10	C(6)C(7)'	-x, -y, 2-z	3.41	-	3.54
	C(7)N(1)'	1 + x, y, z	3.58	-	3.41
	H(7)N(1)'	1 + x, y, z	2.75	149	2.74
	C(7)N(2)'	-x, -y, 1-z	3.37	-	3.41
	H(7)N(2)'	-x, -y, 1-z	2.71	129	2.74
12	Br(1)N(1)'	1 + x, y, 1 + z	3.27	-	3.51
	Br(1)C(9)'	1 + x, y, 1 + z	3.50	_	3.64
	C(7)N(2)'	-x, -y, -z	3.54	_	3.41
	H(7)N(2)'	-x, -y, -z	2.63	166	2.74

On the other hand, the o-Cl, o-Br (**3**, **4**) and o-NO<sub>2</sub> [8] derivatives form centrosymmetric crystal structures. Therefore, search for polymorphism and theoretical modeling of other crystal packing arrays in this series may be important for understanding the 'rules' dictating formation of a given crystal.

Molecular packing diagrams for structures studied are presented in Fig. 6. Several interesting features of the crystal packing mode may be noted. In particular, unit cell parameters of crystals **4** (*o*-Br) and **6** (*m*-F) are very similar (with the same space group), and in both structures molecules form layers along the shortest unit cell parameter *a* (about 3.9 Å, see Table 1). In both crystal structures the C-H...N hydrogen bonds join molecules in the infinite chains along the *c*-crystal axes. The same crystal packing array and unit cell parameters were found earlier for the *o*-Cl derivative **3** [8], so we may consider these compounds as isostructural ones.

For the pair p-F and p-Br (10 and 12), the parameters of the triclinic unit cells are also rather close (but unit cell angles differ more significantly), and molecules in the layer form centrosymmetric dimers via the same C-H...N hydrogen bonds (Fig. 6). On the other hand, molecular superposition in neighboring layers is slightly different: there is no molecular overlap between rings in 10, while some small overlap exists in 12. As a result, geometry of the C-H...N hydrogen bonds in these structures is different (angle at the H atom), and in addition, the second C(7)-H(7)...N(1) H-bond appears in the structure of **10** which connects molecules into infinite chains.

# 3.2. Comparison results of quantum MP2 and DFT calculations

Good agreement between the calculated (MP2 and DFT) and experimental (X-ray) values was obtained for most molecular geometry parameters except the angles of rotation around the C(1)–C(7) bond. The DFT method gives slightly better results for bond angles but very often the MP2/DFT difference is close to the corresponding experimental  $\sigma$ -values. The most significant difference between the two methods was found in description of molecular planarity. For each molecule **1–13** we optimized molecular geometry starting from two models: planar with the symmetry C<sub>s</sub>, and nonplanar with torsion angle C(2)–C(1)–C(7)–C(8) equal to 20°. Some results of computations are listed in Table 7.

Presented data show that MP2 predicts non-planar structures in the case of *ortho*-substituted molecules with noticeable energy difference, while DFT calculations from both starting points result into planar

#### 15



Fig. 6. Molecular packing diagrams for compounds 4–6, 10 and 12.

molecular geometry. It is also obvious that for the *meta-* and *para-substituted* molecules the energy difference between the planar and non-planar structures is negligible (MP2), so there it is no reason to discuss different results of two methods in the two latter cases. Nevertheless, inconsistency of the DFT method for description of conjugated molecules that was emphasized before [29] should be also pointed out for *ortho-substituted* molecules.

# 3.3. Evaluation of NLO properties

Fig. 7 and Table 8 present evaluation of the molecular hyperpolarizability ( $\beta$ ) for the compounds of interest calculated with molecular geometry parameters obtained by the MM (for planar and non-planar conformations), *ab initio* (MP2), and X-ray methods. Table 8 contains also calculated dipole moments ( $\mu$ ) and third-order polarizabilities ( $\gamma$ )

M.Yu. Antipin et al. / Journal of Molecular	Structure 6	50 (2003	) 1–20
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Table 7 Energy difference for planar (pl) and non-planar (npl) conformations of molecules 1-13

Molecule	Method	τ C(6)–C(1)– C(7)–C(8)(°)	$\Delta E(\text{kcal/mol})$
1	MP2	23.1	0.10
	B3LYP	0.0	_
2	MP2	24.1	0.13
	B3LYP	0.0	_
3	MP2	37.5	0.96
	B3LYP	3.2	0.01
4	MP2	38.4	1.08
	B3LYP	0.0	_
5	MP2	49.8	1.51
	B3LYP	0.0	_
6	MP2	24.8	0.13
	B3LYP	0.0	_
7	MP2	24.7	0.12
	B3LYP	0.0	_
8	MP2	24.8	0.12
	B3LYP	0.0	_
9	MP2	32.2	0.06
	B3LYP	0.0	_
10	MP2	19.7	0.05
	B3LYP	0.0	_
11	MP2	19.3	0.04
	B3LYP	0.0	_
12	MP2	19.7	0.04
	B3LYP	0.0	_
13	MP2	0.0	_
	B3LYP	0.0	-

together with available experimental values for the  $\beta$ 's. All methods give quite similar results: in accord with the substituent position molecular hyperpolarizability slightly increases in the sequence of the *ortho*  $\rightarrow$  *meta*  $\rightarrow$  *para* substituted molecules. This may be explained by the lower molecular planarity and shortest possible length of conjugation in the case of *ortho*-substituted compounds. The similar effect was described before for the series of methoxy-substituted dicianovinylbenzenes by theoretical calculations and experimental EFISH measurements [6, 7], but in our case this tendency is much weaker because of electron-acceptor properties of the halogen substituents (in contrast to the donor properties of the OMe-group).

Molecules 4 and 5 have the lowest hyperpolarizabilities due to their largest non-planarity. Introduction of the halogen substituent in the 4-position of the aromatic ring (molecules 10-13) results in higher hyperpolarizability. Planar molecular structure and better conditions for electron conjugation and charge transfer result in larger values of  $\beta$  and  $\gamma$ in this series. *Meta*-substituted molecules (6-9) have the same magnitudes of  $\beta$  and  $\gamma$  as unsubstituted compound (1).

There are only four experimental  $\beta$  values available for this series (Table 8) which were obtained in solution by EFISH technique [8].



Fig. 7. Calculated second order polarizabilities  $\beta$  (10<sup>-51</sup> cm<sup>3</sup> V<sup>-2</sup>) of molecule 1–13.



M.Yu. Antipin et al. / Journal of Molecular Structure 650 (2003) 1–20

Table 8 Calculated dipole moments ( $\mu$ , D), second-order polarizabilities  $\beta$  (10<sup>-51</sup> Cm<sup>3</sup> V<sup>-2</sup>) and  $\gamma$  (10<sup>-61</sup> Cm<sup>4</sup> V<sup>-3</sup>) for molecules 1–13

Molecule <sup>a</sup>	Method	$\mu$	β	γ	Exptl $\beta$
1	MM3-npl	4.396	10.961	3.060	
	MP2	4.641	13.831	3.765	
	X-ray	4.646	12.889	3.505	22.75
2	MM3-npl	4.371	8.186	2.966	
	MP2	4.639	10.596	3.753	
	X-ray	4.320	10.030	3.625	34.16
3	MM3-npl	4.197	6.933	2.761	
	MP2	4.357	8.629	3.325	
	X-ray	4.151	9.915	3.588	36.38
4	MM3-npl	4.117	6.282	2.639	
	MP2	4.285	8.019	3.265	
	X-ray	3.932	7.871	3.076	
5	MM3-npl	4.080	5.938	2.441	
	MP2	4.213	5.660	2.383	
	X-ray	3.903	8.363	3.176	
6	MM3-npl	2.933	10.186	3.061	
	MP2	3.098	12.062	3.755	
	X-ray	2.892	10.530	3.509	
7	MM3-npl	3.150	11.394	3.352	
	MP2	3.322	13.661	4.121	
8	MM3-npl	3.130	11.392	3.404	
	MP2	3.301	13.648	4.189	
9	MM3-npl	3.162	11.884	3.374	
	MP2	3.251	13.295	3.930	
10	MM3-npl	3.210	15.393	3.645	
	MP2	3.441	20.042	4.689	
	X-ray	3.071	16.616	3.944	
11	MM3-npl	3.310	17.509	4.320	
	MP2	3.528	22.859	5.715	
	X-ray	3.242	18.706	4.492	46.40
12	MM3-npl	3.241	16.903	4.495	
	MP2	3.430	21.808	5.924	
	X-ray	3.189	19.055	5.231	
13	MM3-npl	3.241	15.908	4.320	
	MP2	3.416	21.297	6.032	

<sup>a</sup> Obtained from MM3, MP2 calculations and X-ray geometry (X-ray); npl: non-planar.

<sup>b</sup> Experimental data were obtained by the EFISH method in solution (chloroform), see Refs. [6,8] for details.

The difference between the calculated and experimental  $\beta$  values might be explained by the solvent and dispersion effects. A comparison has been done earlier between the calculated and experimental  $\beta$ values for different series of organic compounds (in particular, methoxy-derivatives of dicyanovinylbenzene [6,7], Schiff's bases [30], *p*-nitroaniline derivatives [23], and some others) which resulted in correction factors between 2.0 and 3.4. Although the present data are not sufficient, they give some clue to estimate approximately the order of the molecular  $\beta$  values in solutions. In present case, the correction factors (experimental  $\beta$ /calculated  $\beta$ ) are in the vicinity of 1.5 (molecule 1), 3.5 (molecule 2 and 3) and 2.0 (molecule 11). Some recent approaches to estimate solvent effects on the molecular hyperpolarizabilities are considered, in particular, in [31].

As we noted earlier, compound 5 forms acentric crystals with the space group Pna2<sub>1</sub> and therefore it is active in the SHG in the solid (powder) state. Our measurements have shown that the efficiency of the compound 5 (despite rather small molecular NLO response) is about 5 times more than that for urea, and this compound is phase-matchable. Using the locally written NLOP program [32], the angle between the crystal polar axis c and vectorial part of the  $\beta$  value was calculated and it was found to be equal to 58.8° which is very close to the optimal value 54.7° [11,12]. The fragment of the crystal packing of 5 along with the orientation of the  $\beta$ 's vectorial part is presented in Fig. 8.

So, three compounds of the series studied (2, 5 and 11) were found to be active in the SHG in the solid state with the efficiency about 12, 5 and 20 times more than that of urea as a reference compound. The data of Table 8 along with crystal data for these compounds allow one to understand and explain this difference. Compound 11 has the largest calculated molecular  $\beta$  value in this series (about 3 times more than that for 5) and molecular packing array (space group P2<sub>1</sub>) is close to the optimal one [8]. Compound 2 (space group Pc) is less active than 11 and more active than 5 (because of larger  $\beta$  value). Corresponding EFISH data for 11 and 2 are in line with this observation.

# 4. Supporting information available

Tables of the X-ray structure determination summary, tables of the non-hydrogen atoms coordinates and their anisotropic displacement parameters, tables of hydrogen atoms coordinates and their



Fig. 8. Fragment of crystal packing of 5 along with the orientation of vectorial part of molecular hyperpolarizability.

isotropic displacement parameters, bond lengths, bond angles, and torsion angles.

#### Acknowledgements

We gratefully acknowledge financial support of this research by NASA grant NAG8-1708, and NASA cooperative agreement NCC8-195-A. We also thank K.Suponitsky for his help with quantum chemical calculations.

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