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Structural characterization of monomers for non-linear optical polymers. X-ray analysis and molecular mechanics calculations of 2-(4-methacryloxy-3-methoxyphenyl)-1,1-dicyanoethylene, 2-(3-methacryloxy-4-methoxyphenyl)-1,1-dicyanoethylene, and 2-(2-methacryloxy-3-methoxyphenyl)-1,1-dicyanoethylene

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Abstract

The results of molecular mechanics calculations, hyperpolarizabilities calculations, synthesis, and X-ray analysis of three monomers for non-linear optical polymers are presented. All monomers are derivatives of dicyanovinylbenzene with methoxy and methacryloxy substituents in different positions (full isomers): 2-(4-methacryloxy-3-methoxyphenyl)-1,1-dicyanoethylene **6a**, 2-(3-methacryloxy-4-methoxyphenyl)-1,1-dicyanoethylene **6b**, and 2-(2-methacryloxy-3-methoxyphenyl)-1,1-dicyanoethylene **6c**. On the basis of structural results for molecules **6a**–**c** and calculations of molecular hyperpolarizability, monomer **6a** was found to be the most prospective candidate for NLO polymer preparation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Non-linear optical polymers; Molecular mechanics calculations; X-ray analysis; Dicyanovinylbenzene derivatives

1. Introduction

The present investigation is part of a program which includes molecular modeling, synthesis, preparation of non-linear optical (NLO) materials, and characterization of their structure and properties. Recently we prepared and characterized a series of substituted phenyl-1,1-dicyanoethylene derivatives [1–4]. Only a few of these compounds have acentric crystal structure with polar molecular orientation that is necessary for second harmonic generation (SHG) in solid state. The latter circumstance makes a preparation of polymer NLO materials containing organic chromophores in the side chains especially attractive, since the requirement of acentricity might be fulfilled in polymers by poling of the materials. The other important properties of the polymers are their stability, better mechanical processing, and easier film formation [5].

In the present work structural investigation of three

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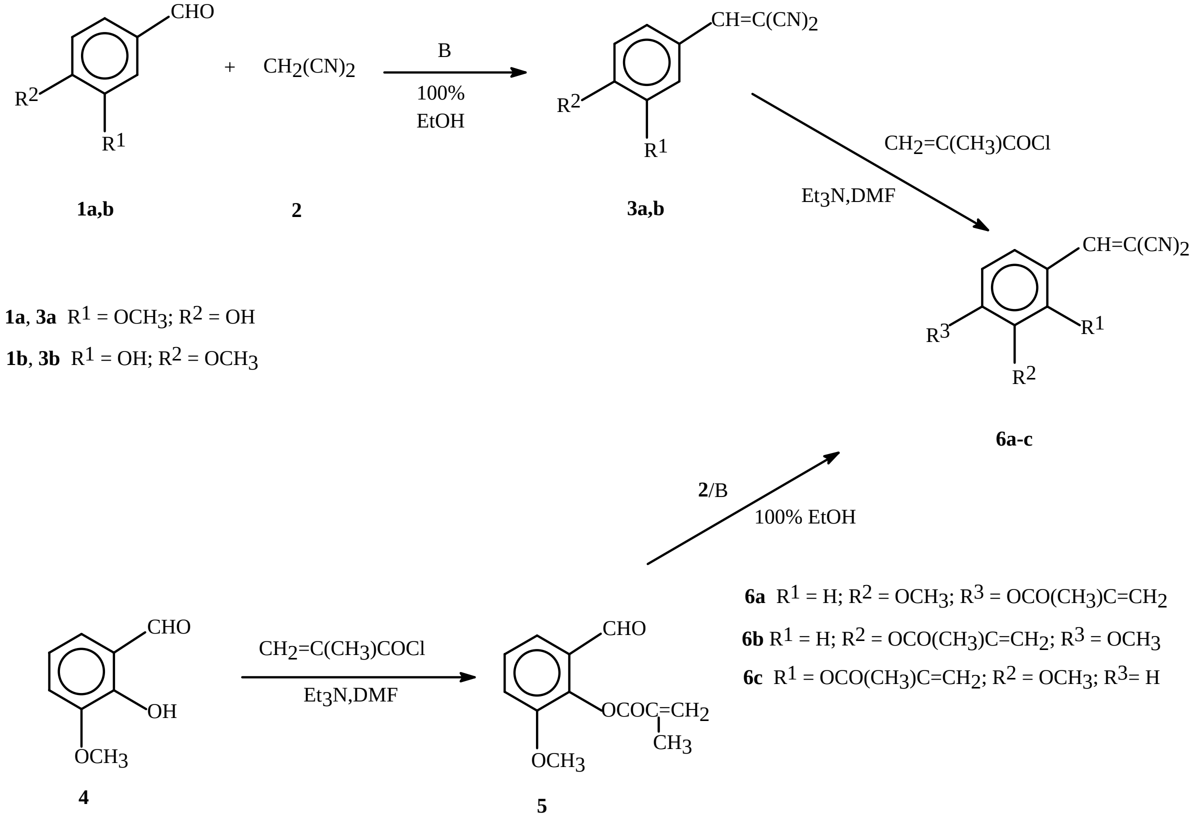
monomers which can form polymers or copolymers of poly(methylmethacrylate) (PMMA) type is presented.

2. Experimental part and calculation details

2.1. Materials

Compounds **3a**, **3b**, **5** and **6a**–**c** have been prepared using the standard procedures described in papers [6–13]. The scheme for the synthesis of these compounds is shown below:



Intermediate compounds and final products have been characterized by ^{1}H NMR and ^{13}C NMR spectra that were collected using a Bruker Model AC 300 MHZ Broad Band High Field FT-NMR Spectrometer.

2-(4-Hydroxy-3-methoxyphenyl)-1,1-dicyanoethylene ***3a****:* The yield of compound **3a** was ca. 85%, (m.p. 134–135°C). ^{1}H NMR ($CDCl_3$) δ; 3.98 (3H, s, OCH_3), 6.44 (1H, w.s, OH), 7.03 (1H, d.d, C_5H), 7.31 (1H, d.d, C_6H), 7.64 (1H, s, C_2H), 7.71 [1H, s, H–C=C$(CN)_2$]. ^{13}C[^{1}H] NMR ($CDCl_3$): δ, 56.2, 78.0, 110.4, 113.6, 114.4, 115.2, 123.9, 128.9, 147.0, 152.1, 159.4.

2-(3-Hydroxy-4-methoxyphenyl)-1,1-dicyanoethylene ***3b****:* The yield of compound **3b** was ca. 90%, (m.p. 249–250°C). ^{1}H NMR (pyridine-d_5) δ, 3.81 (3H, s, OCH_3), 5.02 (1H, w.s, OH), 6.97 (1H, d, C_5H), 7.47 (1H, d, C_6H), 7.96 (1H, s, C_2H), 8.08 [1H, s, H–C=C$(CN)_2$]. ^{13}C[^{1}H] NMR (pyridine d_5): δ, 56.0, 77.7, 112.1, 114.5, 115.6, 116.7, 123.9, 125.4, 148.8, 154.6, 160.5.

2-Methacryloxy-3-methoxybenzaldehyde ***5****:* The yield of compound **5** was ca. 52%, (m.p. 70–71°C). ^{1}H NMR ($CDCl_3$): δ, 2.11 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 5.84 and 6.43 (2H, s, s, CH_2=C, *Z* and *E* isomers), 7.23 (1H, t.d, C_5H), 7.36 (1H, d.d, C_4H), 7.50 (1H, d, C_6H), 10.16 (1H, s, CHO). ^{13}C[^{1}H] NMR ($CDCl_3$): δ, 18.4, 56.3, 117.8, 120.5, 126.7, 128.1, 129.4, 134.9, 142.2, 151.8, 165.0, 188.6.

Table 1
Crystal structure determination summary for compounds **6a**–**c**

	6a	**6b**	**6c**
Empirical formula	$C_{15}H_{12}N_2O_3$	$C_{15}H_{12}N_2O_3$	$C_{15}H_{12}N_2O_3$
Formula weight	268.3	268.3	268.3
Temperature (K)	298(2)	298(2)	298(2)
Crystal size (mm)	0.2 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.4
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	4
Unit cell dimensions			
a (Å)	8.226(2)	6.741(2)	4.896(2)
b (Å)	9.320(3)	10.257(3)	19.710(9)
c (Å)	10.397(3)	10.942(4)	14.652(6)
α (°)	88.32(2)	74.31(2)	90
β (°)	76.16(2)	74.18(2)	93.19(3)
γ (°)	65.04(2)	82.08(2)	90
Volume (Å^3)	699.3(3)	699.2(3)	1412(1)
Density (calc., g/cm^3)	1.274	1.274	1.262
Absorbtion coeff. (mm^{-1})	0.091	0.091	0.090
F(000)	280	280	560
θ range (°)	2.0–25.0	2.0–25.0	2.0–25.0
Scan range ω (°)	1.80	1.90	1.80
Reflections collected	2664	2566	2806
Independent reflections	2475	2333	2495
Data/restraints/parameters	2435/0/229	2299/0/229	2382/0/229
Goodness of fit	1.112	1.033	1.077
Final R/wR [$I > 2\sigma(I)$]	0.056/0.147	0.040/0.095	0.072/0.132
R/wR indices (all data)	0.087/0.187	0.065/0.118	0.169/0.181
Largest difference peak (e/Å^3)	0.30	0.22	0.15
Largest difference hole (e/Å^3)	−0.21	−0.12	−0.17

*2-(4-Methacryloxy-3-methoxyphenyl)-1,1-dicyano-ethylene **6a**:* The yield of compound **6a** was ca. 73% (m.p. 109–110°C). ^{1}H NMR ($CDCl_3$): δ, 2.06 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 5.82 and 6.39 (2H, s, s, $CH_2{=}C$, Z and E isomers), 7.22 (1H, d, C_5H), 7.38 (1H, d, C_2H), 7.70 (1H, d, C_6H), 7.74 [1H, d, H–C=C(CN)$_2$], $^{13}C[^1H]$ NMR ($CDCl_3$): δ, 18.3, 56.1, 82.2, 112.5, 112.7, 113.6, 124.0, 125.6, 128.3, 129.4, 134.9, 145.2, 152.1, 159.0, 164.6.

*2-(3-Methacryloxy-4-methoxyphenyl)-1,1-dicyano-ethylene **6b**:* The yield of compound **6b** was ca. 73% (m.p. 131–132°C). ^{1}H NMR ($CDCl_3$): δ, 2.07 (3H, s, CH_3), 3.93 (3H, s, OCH_3), 5.81 and 6.38 (2H, s, s, $CH_2{=}C$, Z and E isomers), 7.10 (1H, d, C_5H), 7.63 (1H, d, C_2H), 7.72 (1H, d, C_6H), 7.83 [1H, d, H–C=C(CN)$_2$], $^{13}C[^1H]$ NMR ($CDCl_3$): δ, 18.3, 56.4, 79.7, 112.6, 112.9, 114.1, 123.9, 125.1, 128.2, 131.5, 134.9, 140.5, 156.7, 158.1, 164.8.

*2-(2-Methacryloxy-3-methoxyphenyl)-1,1-dicyano-ethylene **6c**:* The yield of compound **6c** was ca. 79% (m.p. 144–145°C). ^{1}H NMR ($CDCl_3$): δ, 2.09 (3H, s, CH_3), 3.86 (3H, s, OCH_3), 5.88 and 6.43 (2H, s, s, $CH_2{=}C$, Z and E isomers), 7.21 (1H, d, C_4H), 7.36 (1H, t.d, C_5H), 7.85 (1H, d, C_6H), 7.88 [1H, d, H–C=C(CN)$_2$]. $^{13}C[^1H]$ NMR ($CDCl_3$): δ, 18.3, 56.3, 84.9, 112.1, 113.6, 117.9, 119.5, 125.2, 127.2, 129.0, 134.5, 140.3, 151.7, 153.3, 164.5.

2.2. X-ray analysis

Single crystals of **6a**–**c** suitable for X-ray analysis were obtained by slow evaporation from ethanol. Single crystalline samples of **6a**–**c** are colorless needles. The experimental data were obtained at room temperature using MoKα-radiation and a graphite monochromator ($\lambda = 0.7107$ Å) with

Table 2
Atomic coordinates ($\times 10^4$) and their equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in structure **6a**

Atom	*x*	*y*	*z*	*U*(eq)[a]
O(1)	2800(2)	8717(2)	3162(2)	75(1)
O(2)	1699(3)	8281(2)	1506(2)	89(1)
O(3)	5372(3)	5881(2)	1937(2)	83(1)
N(1)	2803(4)	−232(3)	6747(2)	92(1)
N(2)	−533(4)	4759(3)	8245(3)	107(1)
C(1)	2895(3)	4575(3)	4837(2)	58(1)
C(2)	4177(3)	4494(3)	3647(2)	60(1)
C(3)	4154(3)	5843(3)	3067(2)	62(1)
C(4)	2810(3)	7315(3)	3681(2)	63(1)
C(5)	1539(4)	7419(3)	4858(2)	67(1)
C(6)	1569(3)	6064(3)	5437(2)	64(1)
C(7)	3045(3)	3070(3)	5338(2)	60(1)
C(8)	2068(3)	2715(3)	6435(2)	60(1)
C(9)	2459(3)	1080(3)	6630(2)	69(1)
C(10)	611(4)	3861(3)	7440(3)	72(1)
C(11)	2252(3)	9062(3)	2011(2)	66(1)
C(12)	2412(3)	10520(3)	1489(2)	67(1)
C(13)	3179(6)	11244(4)	2056(5)	107(1)
C(14)	1655(9)	11060(6)	336(5)	121(1)
C(15)	6608(6)	4390(5)	1199(4)	104(1)
H(2)	5051(32)	3524(29)	3250(22)	57(6)
H(5)	628(36)	8483(32)	5274(25)	75(7)
H(6)	714(41)	6187(32)	6215(30)	82(8)
H(7)	4003(35)	2114(30)	4802(24)	68(6)
H(131)	3287(48)	12053(44)	1607(35)	113(11)
H(132)	3713(63)	10839(52)	2887(46)	152(15)
H(141)	1847(51)	11957(50)	2(36)	121(11)
H(142)	2455(68)	10123(62)	−344(50)	160(18)
H(143)	343(112)	11118(81)	555(68)	230(30)
H(151)	7258(58)	4661(46)	442(45)	134(13)
H(152)	5903(54)	3833(46)	921(37)	125(13)
H(153)	7449(54)	3567(46)	1780(39)	125(12)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and their equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in structure **6b**

Atom	*x*	*y*	*z*	*U*(eq)
O(1)	1973(2)	2467(1)	2702(1)	53(1)
O(2)	4292(2)	1924(1)	986(1)	74(1)
O(3)	1688(2)	4926(1)	1129(1)	63(1)
N(1)	10505(3)	3013(2)	6364(2)	81(1)
N(2)	5644(4)	720(3)	6218(3)	134(1)
C(1)	5884(3)	4103(2)	3440(2)	50(1)
C(2)	4592(3)	3125(2)	3462(2)	49(1)
C(3)	3271(3)	3440(2)	2666(2)	47(1)
C(4)	3110(3)	4732(2)	1832(2)	50(1)
C(5)	4404(3)	5698(2)	1786(2)	54(1)
C(6)	5774(3)	5376(2)	2568(2)	53(1)
C(7)	7355(3)	3891(2)	4235(2)	54(1)
C(8)	7677(3)	2869(2)	5235(2)	57(1)
C(9)	9256(3)	2935(2)	5866(2)	62(1)
C(10)	6527(4)	1683(2)	5775(2)	80(1)
C(11)	2654(3)	1761(2)	1755(2)	50(1)
C(12)	1181(3)	799(2)	1800(2)	59(1)
C(13)	−714(4)	806(3)	2566(4)	102(1)
C(14)	1966(6)	−127(3)	953(3)	97(1)
C(15)	1407(4)	6255(2)	302(3)	67(1)
H(2)	4648(25)	2217(19)	4012(17)	54(5)
H(5)	4316(27)	6534(20)	1230(18)	60(5)
H(6)	6678(29)	6066(19)	2535(17)	66(5)
H(7)	8201(31)	4663(22)	4010(20)	75(6)
H(131)	−1228(58)	1358(38)	3039(38)	162(15)
H(132)	−1509(44)	174(31)	2488(26)	119(9)
H(141)	862(41)	−650(29)	991(25)	112(9)
H(142)	2568(54)	425(34)	−40(37)	146(12)
H(143)	3687(67)	−392(44)	755(42)	199(17)
H(151)	886(34)	6880(23)	826(21)	79(7)
H(152)	271(36)	6200(22)	−62(22)	85(7)
H(153)	2677(39)	6520(23)	−363(23)	82(7)

Siemens P3/PC 4-circle automatic diffractometer using the $\theta/2\theta$-scan technique. The structures were solved by direct methods and refined by a full-matrix least-squares procedure in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were unambiguously located on a difference Fourier map and refined in isotropic approximation. All calculations were carried out with a personal computer using the SHELXTL PLUS program package [14]. Important details of the data collection and structure refinement are summarized in Table 1. Atomic coordinates and their isotropic equivalent displacement parameters are given in Tables 2–4. Bond lengths and bond angles are presented in Tables 5–7.

2.3. Molecular mechanics and hyperpolarizability calculations

Molecular mechanics (MM) calculations of the isomers **6a**–**c** were performed using the MM3 program. For every isomer several most probable conformations corresponding to energy minima were found using a stochastic search procedure [15]. For the calculations of molecular polarizabilities a modification of the static field method [16] developed in Refs. [17,18] was used: 252 static-field calculations

Table 4
Atomic coordinates ($\times 10^4$) and their equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) in structure **6c**

Atom	*x*	*y*	*z*	*U*(eq)
O(1)	1020(4)	5552(1)	2358(1)	53(1)
O(2)	4220(5)	5512(1)	1334(2)	80(1)
O(3)	5160(4)	5470(1)	3578(1)	69(1)
N(1)	−6456(7)	7063(2)	111(2)	90(1)
N(2)	−607(10)	8500(2)	1185(2)	119(1)
C(1)	979(5)	6774(1)	2441(2)	48(1)
C(2)	2132(5)	6156(1)	2714(2)	48(1)
C(3)	4271(6)	6110(2)	3378(2)	52(1)
C(4)	5263(7)	6696(2)	3785(2)	59(1)
C(5)	4121(7)	7313(2)	3523(2)	66(1)
C(6)	2030(7)	7361(2)	2871(2)	61(1)
C(7)	−1295(6)	6766(2)	1756(2)	49(1)
C(8)	−2353(6)	7272(2)	1242(2)	54(1)
C(9)	−4631(7)	7154(2)	611(2)	66(1)
C(10)	−1336(8)	7956(2)	1229(2)	76(1)
C(11)	2344(7)	5244(1)	1668(2)	52(1)
C(12)	1097(7)	4585(2)	1419(2)	62(1)
C(13)	1932(11)	4298(2)	627(3)	103(2)
C(14)	−759(12)	4280(2)	2002(4)	110(2)
C(15)	7328(8)	5391(3)	4265(3)	76(1)
H(4)	6834(57)	6681(14)	4230(19)	57(8)
H(5)	4712(57)	7683(15)	3789(20)	58(9)
H(6)	1235(58)	7756(16)	2721(19)	61(9)
H(7)	−2105(57)	6337(15)	1661(19)	59(8)
H(131)	3064(77)	4551(19)	224(27)	102(13)
H(132)	1179(73)	3875(20)	459(26)	103(13)
H(141)	−1549(85)	3849(23)	1820(28)	120(14)
H(142)	−1989(90)	4541(22)	2254(29)	113(16)
H(143)	767(155)	4122(43)	2640(56)	273(39)
H(151)	7650(78)	4900(23)	4252(27)	110(15)
H(152)	6806(64)	5613(16)	4846(25)	80(11)
H(153)	8983(71)	5624(17)	4041(23)	85(11)

were obtained (MOPAC program, AM1), which were analyzed by the HYPER program [19]. Molecular geometries obtained by molecular mechanics and X-ray analysis were used to calculate molecular polarizabilities.

3. Results and discussion

Table 5
Bond lengths (Å) and bond angles (°) in molecule **6a**

O(1)–C(11)	1.361(3)	C(11)–O(1)–C(4)	115.9(2)
O(1)–C(4)	1.396(3)	C(3)–O(3)–C(15)	116.7(2)
O(2)–C(11)	1.195(3)	C(6)–C(1)–C(2)	118.9(2)
O(3)–C(3)	1.360(3)	C(6)–C(1)–C(7)	125.0(2)
O(3)–C(15)	1.432(4)	C(2)–C(1)–C(7)	116.1(2)
N(1)–C(9)	1.142(3)	C(3)–C(2)–C(1)	121.4(2)
N(2)–C(10)	1.134(3)	O(3)–C(3)–C(2)	125.4(2)
C(1)–C(6)	1.398(3)	O(3)–C(3)–C(4)	115.9(2)
C(1)–C(2)	1.401(3)	C(2)–C(3)–C(4)	118.7(2)
C(1)–C(7)	1.447(3)	C(5)–C(4)–C(3)	120.8(2)
C(2)–C(3)	1.373(3)	C(5)–C(4)–O(1)	118.6(2)
C(3)–C(4)	1.394(3)	C(3)–C(4)–O(1)	120.5(2)
C(4)–C(5)	1.382(3)	C(6)–C(5)–C(4)	120.3(2)
C(5)–C(6)	1.377(3)	C(5)–C(6)–C(1)	119.9(2)
C(7)–C(8)	1.349(3)	C(8)–C(7)–C(1)	131.7(2)
C(8)–C(10)	1.434(4)	C(7)–C(8)–C(10)	124.8(2)
C(8)–C(9)	1.437(3)	C(7)–C(8)–C(9)	119.2(2)
C(11)–C(12)	1.493(3)	C(10)–C(8)–C(9)	116.0(2)
C(12)–C(13)	1.327(4)	N(1)–C(9)–C(8)	177.9(3)
C(12)–C(14)	1.462(5)	N(2)–C(10)–C(8)	179.3(3)
		O(2)–C(11)–O(1)	122.9(2)
		O(2)–C(11)–C(12)	125.3(2)
		O(1)–C(11)–C(12)	111.8(2)
		C(13)–C(12)–C(14)	124.1(3)
		C(13)–C(12)–C(11)	121.3(3)
		C(14)–C(12)–C(11)	114.7(3)

A stochastic search of the preferable conformers of the molecules **6a**–**c** has shown that for all molecules studied several conformations with different orientations of substituents are possible. For instance, for monomer **6a** 11 conformers with energy difference less than 1.0 kcal/mol were found, for monomers **6b** and **6c**, respectively, 22 and 17 possible conformers were found in the same energy interval. The energy differences (in kcal/mol) between the most energetically preferable conformers and conformers corresponding to the X-ray structures are equal to 0.72 (**6a**), 0.56 (**6b**), and 0.04 (**6c**), respectively. For some of these conformers the geometry differences are rather small (**6c**), while the other conformers (**6a** and **6b**) differ significantly due to the substituents orientations. The most energetically preferable conformers of molecules **6a**–**c** found as a result of stochastic search are shown in Fig. 1.

Molecular crystal structures of isomers **6a**–**c** are presented in Fig. 2. Comparison of Figs. 1 and 2 shows the difference between conformations of isolated molecules and molecules in crystals. One can see that calculated and X-ray conformations of molecule **6c** resemble each other while for molecules **6a** and **6b** they differ significantly.

Because of small energy difference for isolated and solid state conformers (see above), we can suggest

Table 6
Bond lengths (Å) and bond angles (°) in molecule **6b**

O(1)–C(11)	1.365(2)	C(11)–O(1)–C(3)	115.67(13)
O(1)–C(3)	1.401(2)	C(4)–O(3)–C(15)	117.88(14)
O(2)–C(11)	1.193(2)	C(6)–C(1)–C(2)	117.9(2)
O(3)–C(4)	1.349(2)	C(6)–C(1)–C(7)	117.0(2)
O(3)–C(15)	1.438(2)	C(2)–C(1)–C(7)	125.1(2)
N(1)–C(9)	1.143(2)	C(3)–C(2)–C(1)	119.9(2)
N(2)–C(10)	1.145(3)	C(2)–C(3)–C(4)	121.9(2)
C(1)–C(6)	1.400(2)	C(2)–C(3)–O(1)	119.70(14)
C(1)–C(2)	1.407(2)	C(4)–C(3)–O(1)	118.3(2)
C(1)–C(7)	1.448(3)	O(3)–C(4)–C(5)	125.4(2)
C(2)–C(3)	1.360(2)	O(3)–C(4)–C(3)	115.99(14)
C(3)–C(4)	1.401(2)	C(5)–C(4)–C(3)	118.6(2)
C(4)–C(5)	1.390(2)	C(6)–C(5)–C(4)	119.7(2)
C(5)–C(6)	1.374(3)	C(5)–C(6)–C(1)	121.9(2)
C(7)–C(8)	1.338(3)	C(8)–C(7)–C(1)	131.4(2)
C(8)–C(10)	1.432(3)	C(7)–C(8)–C(10)	125.2(2)
C(8)–C(9)	1.435(3)	C(7)–C(8)–C(9)	119.5(2)
C(11)–C(12)	1.476(2)	C(10)–C(8)–C(9)	115.2(2)
C(12)–C(13)	1.323(3)	N(1)–C(9)–C(8)	178.7(2)
C(12)–C(14)	1.453(3)	N(2)–C(10)–C(8)	178.5(2)
		O(2)–C(11)–O(1)	121.8(2)
		O(2)–C(11)–C(12)	124.9(2)
		O(1)–C(11)–C(12)	113.3(2)
		C(13)–C(12)–C(14)	123.7(2)
		C(13)–C(12)–C(11)	121.1(2)
		C(14)–C(12)–C(11)	115.3(2)

Table 7
Bond lengths (Å) and bond angles (°) in molecule **6c**

O(1)–C(11)	1.373(4)	C(11)–O(1)–C(2)	117.5(2)
O(1)–C(2)	1.397(3)	C(3)–O(3)–C(15)	117.9(3)
O(2)–C(11)	1.188(3)	C(2)–C(1)–C(6)	117.4(3)
O(3)–C(3)	1.361(3)	C(2)–C(1)–C(7)	118.1(3)
O(3)–C(15)	1.429(4)	C(6)–C(1)–C(7)	124.5(3)
N(1)–C(9)	1.137(4)	C(1)–C(2)–C(3)	122.4(3)
N(2)–C(10)	1.135(4)	C(1)–C(2)–O(1)	119.7(2)
C(1)–C(2)	1.392(4)	C(3)–C(2)–O(1)	117.9(3)
C(1)–C(6)	1.402(4)	O(3)–C(3)–C(4)	125.7(3)
C(1)–C(7)	1.457(4)	O(3)–C(3)–C(2)	115.5(2)
C(2)–C(3)	1.393(4)	C(4)–C(3)–C(2)	118.8(3)
C(3)–C(4)	1.377(4)	C(3)–C(4)–C(5)	119.3(3)
C(4)–C(5)	1.383(5)	C(6)–C(5)–C(4)	122.2(3)
C(5)–C(6)	1.364(5)	C(5)–C(6)–C(1)	119.9(3)
C(7)–C(8)	1.338(4)	C(8)–C(7)–C(1)	129.6(3)
C(8)–C(9)	1.428(5)	C(7)–C(8)–C(9)	120.5(3)
C(8)–C(10)	1.437(5)	C(7)–C(8)–C(10)	125.7(3)
C(11)–C(12)	1.472(4)	C(9)–C(8)–C(10)	113.8(3)
C(12)–C(13)	1.374(5)	N(1)–C(9)–C(8)	179.5(3)
C(12)–C(14)	1.415(6)	N(2)–C(10)–C(8)	177.0(4)
		O(2)–C(11)–O(1)	120.9(3)
		O(2)–C(11)–C(12)	127.6(3)
		O(1)–C(11)–C(12)	111.5(3)
		C(13)–C(12)–C(14)	124.4(4)
		C(13)–C(12)–C(11)	115.7(4)
		C(14)–C(12)–C(11)	119.8(3)

that intermolecular interactions in the crystals are mostly responsible for the solid state molecular conformations at least for compounds **6a** and **6b**.

According to the X-ray analysis, molecules **6a**–**c** have similar geometry, however they are also characterized by different features due to different positions of substituents in the benzene ring which will be described below. For instance, the dihedral angles between the dicyanovinyl group and the benzene ring are equal to 5.1 (**6a**), 9.0 (**6b**) and 19.6° (**6c**). For molecules **6a** and **6b** these values belong to the standard interval (0–15°) of such angles in the other molecules with the dicyanovinyl group studied before (see Ref. [4]), where there is no influence of the bulky substituents in the *ortho*-positions [4,20]. In molecules with such substituents, for instance, in *ortho*-pyrrolidino-dicyanovinylbenzene, the dihedral angle between the dicyanovinyl group and the benzene ring is larger (21.9°) [20], and the latter value is close to that found in molecule **6c**. We should note several short intramolecular contacts between substituents in *ortho*-positions in molecule **6c** responsible for non-planar orientation of the dicyanovinyl group, such as O(1)···C(7) 2.770(4), and O(1)···H(7) 2.37(3) Å, and a short contact between carbon atom of the nitrile group and hydrogen atom of the benzene ring C(10)···H(6) 2.49(3) Å. The methoxy substituents in molecules **6a**–**c** are in a position *ortho* to the bulky methacrylocarboxy substituent. Nevertheless, out-of-plane displacements of the methoxy groups are insignificant: 8.5° in **6a**, 3.5° in **6b**, and 1.0° in **6c**. Significant out-of-plane displacement of the methoxy group was found only for molecules where the OMe group is located between two other substituents, for instance in 3,4,5-trimethoxydicyanovinylbenzene, where the OMe group in position 4 is almost perpendicular to the benzene ring [2]. In all three molecules studied, orientation of the methacryloxy groups to the benzene ring plane are almost perpendicular. Dihedral angles between their planes are equal to 75.6° in **6a**, 89.6° in **6b**, and 91.0° in **6c**. According to the molecular

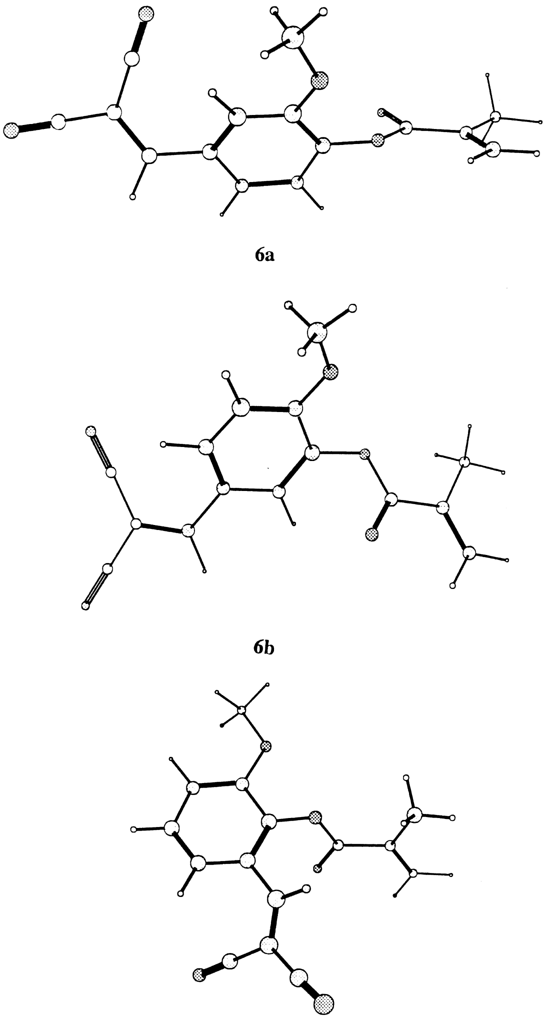


Fig. 1. Calculated conformations of isolated molecules **6a**–**c**.

mechanics calculations, the methacryloxy groups are also significantly rotated out of the benzene ring planes but dihedral angles for calculated molecules are somewhat smaller than in crystals: 56 (**6a**), 49 (**6b**), and 68° (**6c**).

No intermolecular contacts that are significantly shorter than sum of van der Waals radii were found in the crystals **6a**–**c**. Nevertheless it is possible to mention some intermolecular contacts which in our opinion may be responsible for a particular molecular pattern (Fig. 3). For instance, in crystals of **6a** and **6b** the centrosymmetric dimers are formed via contacts between nitrogen atoms of the cyano group and hydrogen atoms of the ethylene group (N(1)···H(7) 2.61 Å in **6a**, and N(1)···H(7) 2.54 Åin **6b**). Similar dimers were also found in dicyanovinylbenzene [1], where the same contacts were equal to 2.56 Å. We suggest that such contacts are due to the electrostatic interactions between positively charged hydrogen atoms H(7) and negatively charged atoms N(1) of the cyano group. Ab initio calculations of charge distribution in several dicyanovinylbenzene derivatives have been presented earlier [4]. Namely formation of centrosymmetric dimers by molecules **6a**, **6b**, and dicyanovinylbenzene [1] is apparently the main reason for the centrosymmetric crystal structure found for these compounds. In Ref. [1] we observed that in same other dicyanovinylbenzene derivatives, substituents in the position *ortho* to the dicyanovinylgroup can prevent the dimer formation, and in some cases this leads to a formation of acentric crystals. For instance, *ortho*-methoxy-dicyanovinylbenzene [1] and *ortho*-fluoro-dicyanovinylbenzene form non-centrosymmetric crystal structures [4]. This observation of course is not general. For instance, molecular dimers of the type mentioned above were not found in *ortho*-chloro-dicyanovinylbenzene [4] and *ortho*-nitro-dicyanovinylbenzene [4], but destruction of the dimers formation is not sufficient enough for acentric structure formation in these cases. The same situation was found for crystal **6c**. There are no molecular dimers in this crystal, but crystal **6c** as well as **6a** and **6b** are centrosymmetric.

Table 8
Calculated dipole moments μ (D), second-order β (10^{-51} C m^3/V^2), and third-order γ (10^{-61} C m^4/V^3) molecular polarizabilities for monomers **6a**–**c**

Molecule	μ	β	γ
6a			
X-ray	4.89	30.16	7.99
MM	4.57	27.00	7.34
6b			
X-ray	6.12	39.37	8.13
MM	4.90	31.44	7.52
6c			
X-ray	5.95	14.74	4.77
MM	5.04	12.24	4.06

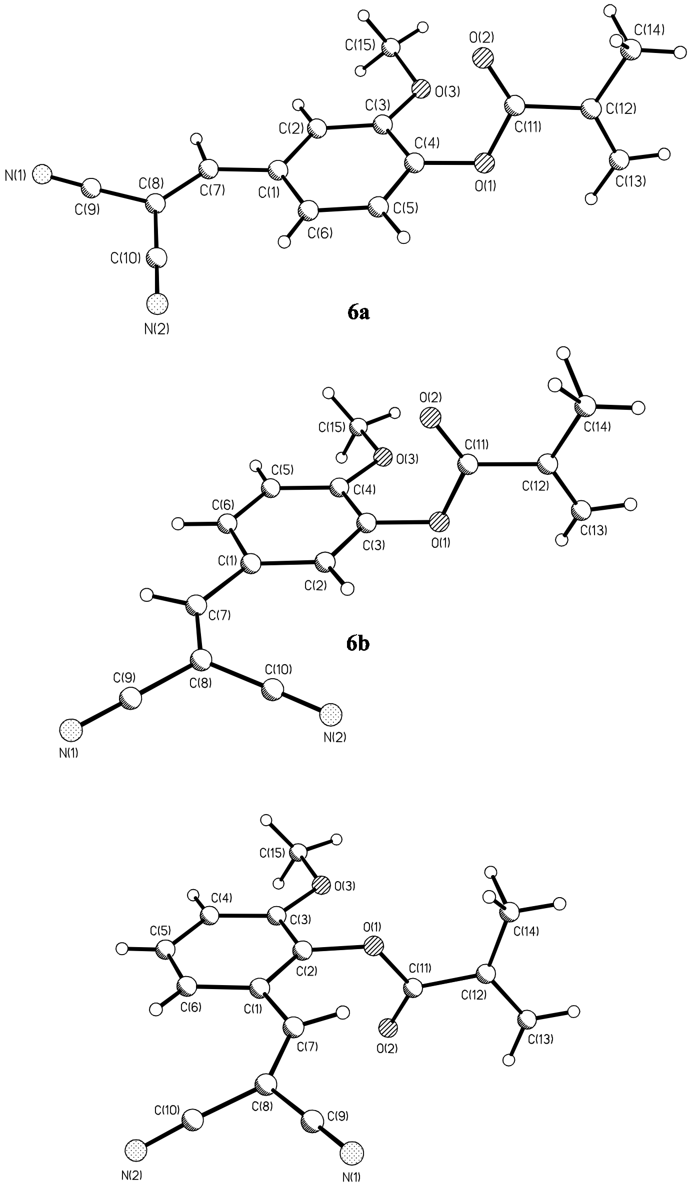
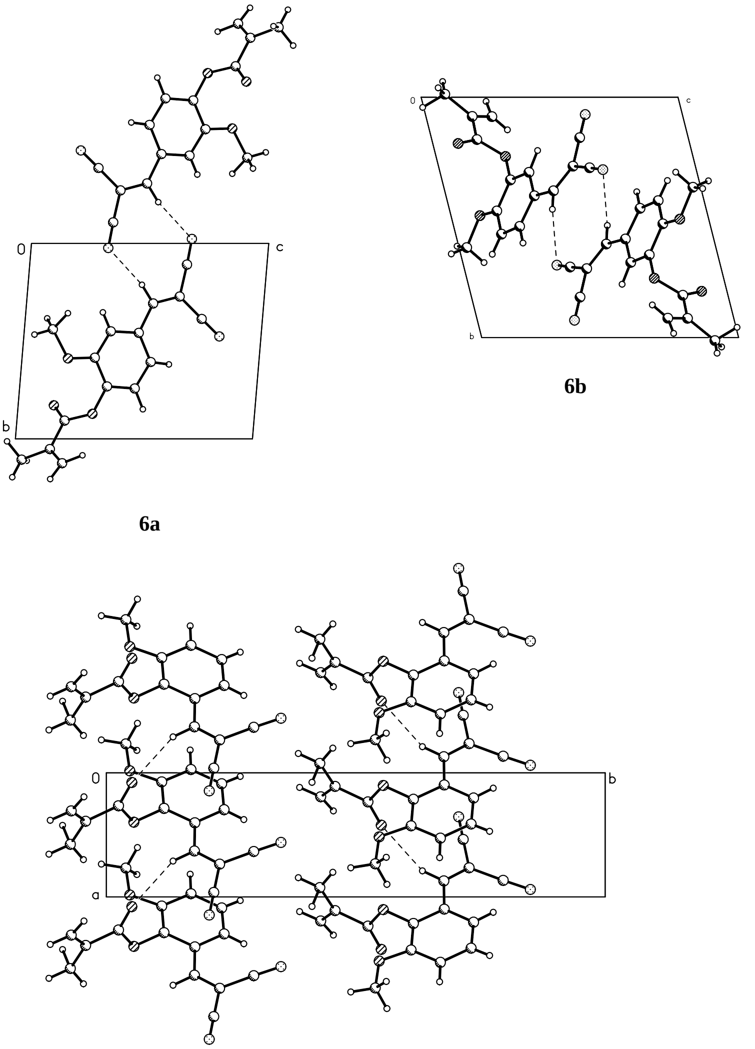


Fig. 2. Molecular structure of compounds **6a**–**c** in crystals.

So, none of the crystals under investigation can demonstrate NLO properties in the solid state.

Results of the molecular dipole moments and hyperpolarizability calculations based on molecular structure from MM calculations (the most energetically preferable conformers) and X-ray data are listed in Table 8. Due to different conformations for isolated molecules and the molecules in crystals the results are somewhat different but definitely show the same trend: β values increase in the series **6c** $<$ **6a** $<$ **6b**. It is obvious that the most important for calculated properties in question



6a

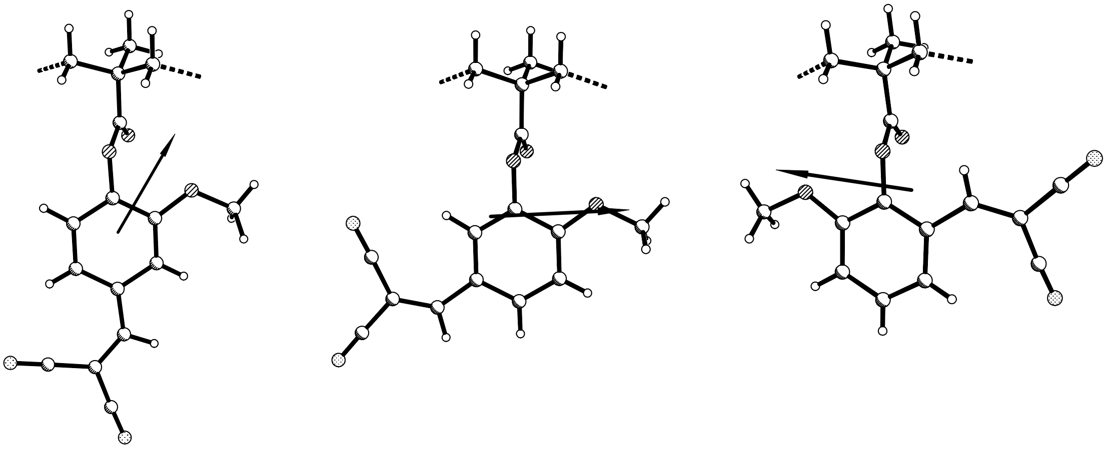
6b

6c

Fig. 3. Projections of molecular packings in crystals **6a**–**c**.

is relative substituents positions in phenyl ring but not their relative orientation. Calculated positions of the side chromophore substituents with respect to polymer backbone direction and relative orientations of the dipole moments are shown in Fig. 4. It is possible to see that it will be easier to orient dipole moments in one direction (for instance by poling) for **6b** and **6c**. As monomer **6b** has a large β value (see above) we believe that this monomer will be the most prospective candidate for NLO polymer preparation.

Supporting information available: Tables of the X-ray structure determination summary, tables of the non-hydrogen atom coordinates and their equivalent displacement parameters, bond lengths, bond angles, anisotropy displacement parameters for non-hydrogen atoms, hydrogen atoms coordinates, and their isotropic displacement parameters.



6a **6b** **6c**

Fig. 4. Orientation of chromophores **6a**–**c** and chromophore dipole moments relative to polymer chain direction (dashed line).

Ordering information is given on any masthead page.

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