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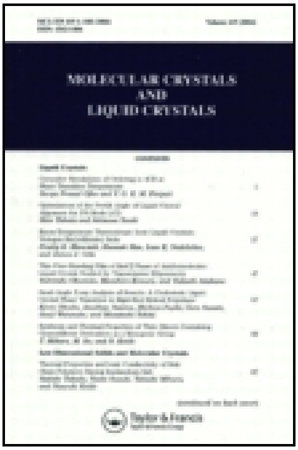

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Molecular Design and Non-Linear Optical Properties in the Series of Substituted Dicyanovinylaromatics

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Molecular Design and Non-Linear Optical Properties in the Series of Substituted Dicyanovinylaromatics

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X-Ray single crystal study, molecular mechanics calculations and quantum-chemical calculations of the static nonlinear optical (NLO) polarizabilities (β) were performed for a large series of dicyanovinylaromatic derivatives in order to make conclusions about the relationship between their molecular geometry, crystal structure and NLO properties. For some compounds studied EFISH measurements of the β values in solutions were made and good correlation was found between the calculated and experimental values. X-Ray data and optimal molecular associate calculations revealed the factors responsible for formation of centric/acentric crystal structures. This approach might be useful for prediction of possible crystal structures for simple organic chromophores. In the series studied only three acentric crystal structures were found, and in agreement with their molecular, electronic and crystal packing characteristics all were found to be active in second harmonic generation (SHG) in the solid state. For the known NLO crystal of dicyanovinylanisole (DIVA), a high-resolution low-temperature (153K) multipole X-ray diffraction analysis of the electron density distribution has been performed, and these data were used for an estimation of the molecular dipole moment and β values directly from the X-ray diffraction data.

Keywords: X-ray analysis; molecular mechanics; nonlinear optics; electron density distribution; dicyanovinylaromatics

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INTRODUCTION

Organic molecular crystals with high optical nonlinearities are the subject of intensive studies because of their possible applications. The traditional way to design of such materials includes, as a rule, preliminary estimation of their nonlinearities using theoretical quantum calculations, chemical synthesis of the compounds of interest, and experimental studies of their crystal structures and NLO properties. An X-ray diffraction analysis is an essential part in such molecular design because this method provides unique information about the structure of compounds, including their molecular geometry, crystal packing, and crystal symmetry. Modern application of this method allows one to obtain additional information about the electron density distribution characteristics in molecules and crystals including those responsible for many NLO properties. We may indicate a few levels of application of the X-ray diffraction analysis in the NLO materials studies.

First, X-ray data provide unequivocal information about crystal symmetry and morphology. Knowledge of the crystal symmetry (space group) is important because only acentric crystals may be active in SHG in the solid state. The "second" level of the X-ray data application is related to analysis of the molecular and crystal structures of compounds under consideration. It is known that orientation of the dipole moment or charge transfer direction in a molecule with respect to the polar crystal axes is a crucial factor influencing the efficiency of the nonlinear optical responses. For a given crystal symmetry there are "optimal" orientation angles,[1] and the closer the molecular dipole moment is to this orientation, the better NLO characteristics of the crystal might be. So, X-ray data provide valuable information about "optimal" crystal structures, and there are examples[2], where the molecular crystal packing array was found to be the best for exhibiting highest NLO characteristics.

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On the other hand, the presense of a very high molecular nonlinear response (say, calculated or measured in solutions) cannot guarantee that even in an acentric crystal the molecule will have an optimal orientation. One such example is the crystal structure of *p*-nitro-dimethylaniline.[3] Therefore molecular modeling and analysis of the factors influencing a given crystal structure is an important part in NLO materials design.

Finally, the "third" level of the application of the X-ray method is related to analysis electron density distribution ρ(r) and its characteristics (atomic charges, multipole moments, etc.), that may be obtained directly from the diffraction measurements.[4] Some of these characteristics are responsible for NLO properties of materials. It has been shown for instance,[5,6] that molecular quadrupole and octopole moments are related to the components of the first- and second-order nonlinear polarizability tensors, that makes this approach very attractive for a prior estimation of the latter quantities.

In the present paper we report X-ray analysis, molecular mechanics calculations, and calculations and measurements of the β values for a series of substituted dicyanovinylaromatic and parent compounds with OMe- and NMe_2-groups in aromatic rings in order to establish a relation between their molecular (and crystal) structure and NLO properties. A list and numbering of compounds studied (**I-XIX**) are given in Table 1.

RESULTS AND DISCUSSION

Crystallographic data for 11 compounds studied by the X-ray method are summarized in Table 2. Table 3 contains calculated dipole moments (μ) and second-order polarizabilities (β) for all compounds studied. For some of them experimental values of β in solutions are available and included in the table. Molecular geometry for quantum chemical calculations was taken from

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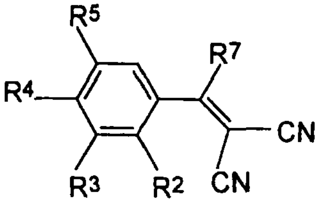
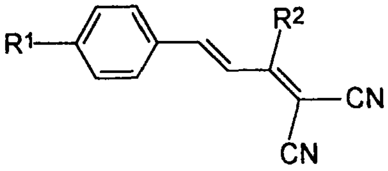
TABLE 1 Substituents positions in the compounds studied



Molecules I-XIII

Molecule	R^2	R^3	R^4	R^5	R^7
I[a]	H	H	H	H	H
II[a] (DIVA)	OMe	H	H	H	H
III	H	OMe	H	H	H
IV[a]	H	H	OMe	H	H
V[a]	OMe	H	OMe	H	H
VI[a]	H	OMe	OMe	H	H
VII[a]	H	OMe	OMe	OMe	H
VIII[a]	H	H	H	H	Ph
IX[a]	OMe	H	H	H	Ph
X	H	H	OMe	H	Ph
XI	NMe_2	H	H	H	H
XII[a]	H	H	NMe_2	H	H
XIII[a]	NO_2	H	H	H	H



Molecules XIV-XIX

Molecule	R^1	R^2
XIV[a]	OMe	H
XV	NMe_2	H
XVI	NEt_2	H
XVII	OMe	CN
XVIII	NMe_2	CN
XIX	NEt_2	CN

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[a] X-ray structures were studied

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MM3 program or from X-ray data, optimal molecular dimers configurations were calculated with the MM3 program using a stochastic search procedure. Quantum-chemical calculations of the μ and β values were performed with MOPAC and HYPER programs.[9] Details of the experimental procedures and calculations are given in ref.[7]

Table 2 shows that only three compounds (DIVA-**II**, **XII** and **XIV**) of the series studied form acentric crystals and therefore may be active in SHG in the solid state. For DIVA and **XII** the second harmonic generation data were reported earlier.[10,11] Our preliminary results for **XIV** have demonstrated that it also gives a rather strong SHG signal in powder. We should note, that as for **XII**, its molecular β value is several times larger than that of DIVA (Table 3).

Data from Table 3 allow one to make some conclusions about the relationship between the molecular structure and NLO characteristics. Thus, the long chain molecules **XIV-XIX** have much larger β values than molecules **I-XIII** with the shorter π-electron conjugation chains. The only exception is compound **XII** having the largest β for dicyanovinylaromatics, that was confirmed by EFISH measurements in solution (1,4-dioxane, λ=1064 nm; for comparison of calculated and measured β values a factor of two was found to be an adjustment parameter to account for the solvent and dispersion effects[7]). As expected, molecular nonplanarity (compounds **VIII**, **IX**, **XI**, **XIII**) results in essential declining in the β values. Data for various OMe-and NMe_2-substituted compounds proved that *o*- and *m*-substitution has small effect on β, while *p*-substitution has the largest effect. Furthermore, an efficiency of the *p*-dimethylamino group is much larger than that of methoxy-group (compare pairs **IV**, **XII** and **XIV**, **XV** in Table 3). X-Ray structures of several compounds studied (**VI**,**VII**,**IX** and **XIV**) are presented in Figure 1.

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TABLE 2 Crystallographic data for compounds studied

Compound	Unit cell dimensions				Space group	Z	R, %
	a, Å	b, Å	c, Å	β[a], deg			
I	9.368(6)	3.916(3)	22.015(15)	93.58(2)	P2$_1$/c	4	5.85
II	7.922(2)	5.402(2)	11.375(2)	97.62(2)	P2$_1$	2	4.22
IV	3.919(2)	24.959(13)	9.671(3)	91.12(2)	P2$_1$/c	4	5.24
V	8.374(3)	7.410(2)	17.149(6)	94.10(2)	P2$_1$/n	4	4.26
VI	7.501(2)	8.892(3)	9.223(2)	93.77(3) 105.44(2) 110.23(2)	P-1	2	4.67
VII	3.914(2)	14.192(7)	22.374(9)	91.35(4)	P2$_1$/c	4	6.97
VIII	9.877(2)	16.258(4)	7.852(2)	91.57(2)	P2$_1$/c	4	4.30
IX	8.394(2)	8.357(2)	20.036(4)	93.97(2)	P2$_1$/n	4	5.44
XII	3.951(2)	14.078(11)	9.499(9)	99.88(8)	P2$_1$	2	9.84
XIII	7.443(2)	19.839(7)	7.023(2)	118.12(1)	P2$_1$/n	4	5.10
XIV	3.957(2)	13.832(4)	10.392(5)	94.11(3)	Pc	2	12.95

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[a]For triclinic structure α, β, and γ values are listed

TABLE 3 Calculated dipole moments (μ, D) and second order polarizabilities (β, 10^{-51} Cm^3 V^{-2}) for molecules I-XVII

Molecule	μ	β	exptl β	Molecule	μ	β	exptl β
I	4.88	16.12	22.75[a]	XI	5.16	8.49	
II	6.81	12.35	18.71[a]	XII	7.21	88.57	145.5 118.7[b]
III	5.70	19.41		XIII	5.86	1.36	
IV	4.96	41.98	56.49[a]	XIV	7.43	103.47	90.9 118.7[b]
V	6.56	35.68	76.27[a]	XV	7.18	136.48	
VI	4.87	51.05		XVI	8.46	198.67	
VII	3.98	37.95		XVII	6.02	106.92	
VIII	4.77	6.52		XVIII	8.44	256.75	
IX	5.99	7.59		XIX	8.52	275.37	
X	5.83	18.53					

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[a]Ref.[7]; [b]Ref [8]

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Crystal packing projections for two non-centrosymmetric structures **XII** and **XIV** down the *a*-axes are shown in Figure 2. Molecular orientation in the crystal of **XII** is favorable for the high NLO response because the angle between the polar *b*-axis and molecular charge transfer direction (or dipole moment orientation) is equal to 59.3°, which is close to the "optimal" value of 54.7° for space group $P2_1$. Note that for DIVA the similar angle is almost the same (59.7°). In the crystal of **XIV** (space group Pc) the angle between the molecular dipole orientation and the *c*-axis is equal to 75.4° and this compound was found also to be rather active in SHG in the solid state. Because molecular nonlinear susceptibilities for **XII** and **XIV** are very high, further studies of their NLO properties may have an interest for applications.

In order to reveal factors responsible for the centric/acentric character of a given structure, available X-ray data for compounds **I**, **II**, **IV-VIII**, **XII** and **XIV** were completed with MM3 calculations of the optimal dimer configurations. Calculations showed that the energy difference between dimers with starting parallel orientation and those having C_i- or C_2-symmetry is significant, so parallel dimers are not preferable in a free state, nor were they found in the crystals studied. On the other hand, the difference between dimers with starting C_i and C_2 symmetries is relatively small (≤ 1 kkal/mol). Nevertheless, some results of these calculations are interesting. Thus, C_i-dimers were found in crystals of **V** and **VI** where strong stacking interactions between planar molecules are responsible for the given crystal structure. For molecules **I**, **IV**, **VII** and **VIII** calculated C_i-dimers are also preferable, but these fragments were not found in crystals, probably because of importance the "in-plane" hydrogen-bond interactions C(7)-H(7)...N≡C, that were not taken into account in calculations, but were found in most structures studied.

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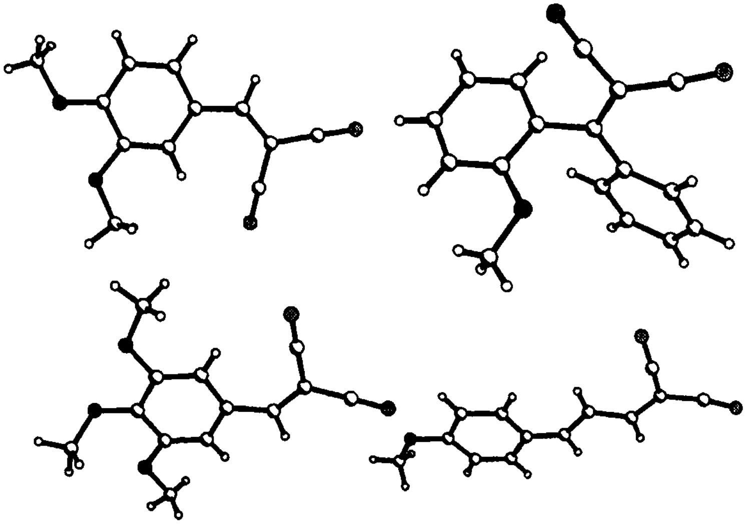

FIGURE 1 Molecular structures of the compounds **VI**, **VII**, **IX** and **XIV**.

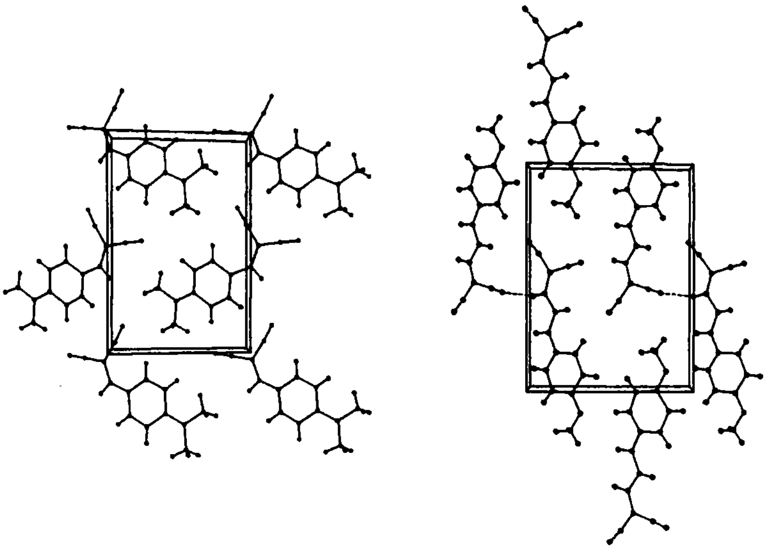

FIGURE 2 Crystal packing projections down the *a*-axes for **XII** and **XIV**.

These weak hydrogen bonds together with stacking interactions probably prevent crystal structure acentricity. Finally, for molecules **II**, **XII** and **XIV** the dimers with C_2 symmetry are more stable, or at least have the same energy as C_i-dimers, and these compounds were found to form acentric crystals. These results show that the described procedure may be used for calculating the structure of possible molecular associates, however its reliability for prediction unknown crystal structures may be considered only as feasible.

Electron density distribution analysis for the DIVA crystal has been performed using high-resolution low temperature (153K) diffraction data and the multipole model.[4] It was first shown by Robinson[6] that the components of the molecular quadrupole and octopole moments (that now may be obtained from the multipole model) are related with the β tensor, and in this work we tried to estimate the β value (and dipole moment) for DIVA directly from X-ray data. A static multipole deformation electron density (DED) map and the map of the electrostatic potential in the molecular plane of DIVA are shown in Figure 3. These data allowed one to detect intramolecular hydrogen bond C(7)-H(7)...O in the molecule (that stabilizes a planar conformation), and non-equivalence of the C≡N-groups. Further topological analysis of the ρ(r) characteristics had demonstrated that there is no "quinoid" contribution in the electronic structure of this molecule. Calculated from the X-ray data dipole moment was found to be 6.6D that is close to the experimental value 6.8D in solution and results of quantum-chemical calculations (Table 2). The direction of the dipole monent in crystal is close to the calculated one in a free molecule. Estimated from the X-ray data the mean value of the β was equal to 58.6 10^{-51} Cm^3V^{-2} which is of the same order of magnitude as the experimental value. Further development of this technique is in progress.

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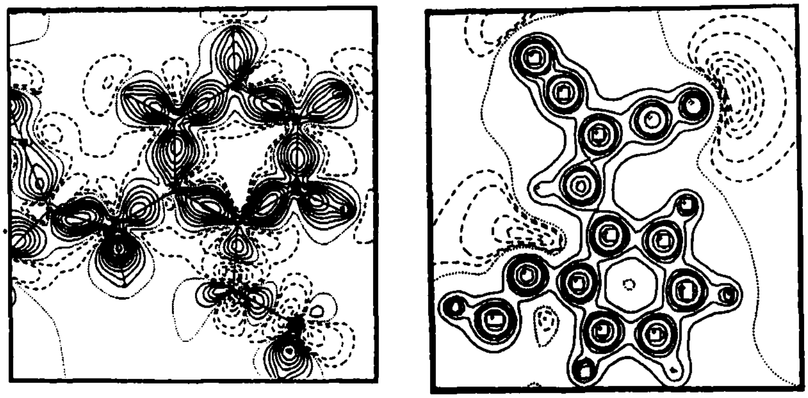

FIGURE 3 DED (left) and electrostatic potential (right) maps in DIVA.

Acknowledgments

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