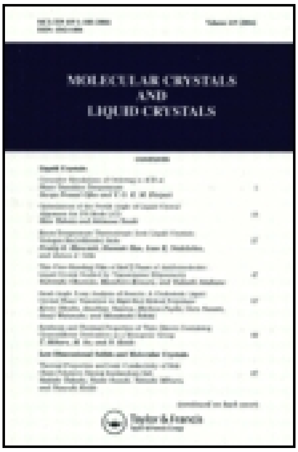

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Second Order Nonlinear Optical Properties of a New Class of Organic Molecules

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Second Order Nonlinear Optical Properties of a New Class of Organic Molecules

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*Linear and nonlinear optical properties of racemic and enantiomerically pure (*R*)-[1-(4-[2.2]paracyclophanyl)]-3-phenylpropane-1,3-diones, the first representatives of a novel class of noncentrosymmetric molecules, namely planar chiral [2.2] paracyclophane derived β-diketones, have been studied. Both molecules exhibit second harmonic generation ability, the efficiency of which was measured by the powder technique at 1064.2 nm fundamental wavelength and their average NLO susceptibility was found comparable with that of a such well known NLO crystal as PNP.*

Keywords β-diketone; [2.2]paracyclophane; luminescence; NLO properties

1. Introduction

The observed development of information society, demanding demand for the volume and higher volume, signal amplification and faster information transfer as well as processing create new challenges and demand new solutions. On the other hand there is an increasing demand for frequency tunable, high power monochromatic beams. One of the possible answers is the use nonlinear optical (NLO) phenomena. Some of them are already in application, e.g. frequency tuning via frequency doubling, optical parametric oscillation (OPO) or sum-difference frequency generation. A very important application, which is the fast, large band electro-optic modulation for optical signal transmission, attracts actually the most of attention. For these, and other, e.g. optical rectification for THz electric pulse generations, otherwise not obtainable by electric circuitries, highly light responsive NLO materials are required. Moreover for the above cited applications based on second order NLO effects the materials to be used have to lack center of symmetry.

Organic molecules emerged as very interesting class of materials for the application in devices based on second order NLO effects. They exhibit high polarizability and fast, electronic in origin, NLO response. The most interesting appeared to be the 1D charge

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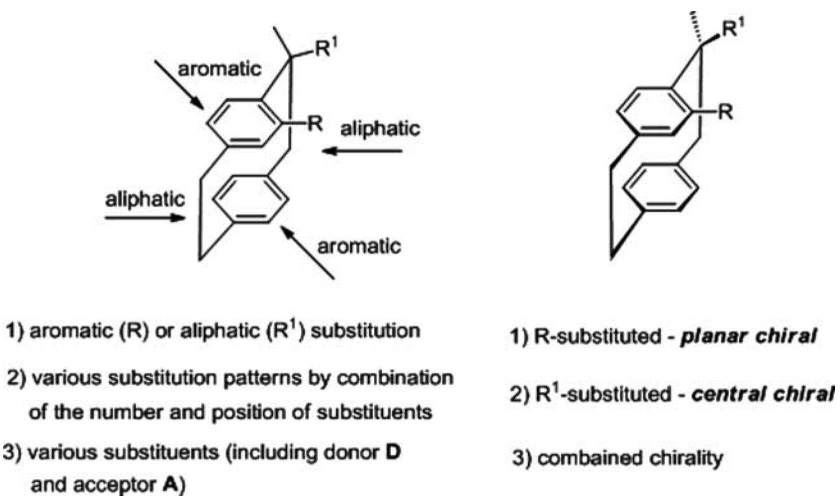
transfer molecules. However these molecules exhibit a large ground state dipole moment. The resulting strong dipole-dipole interaction leads to antiparallel alignement of dipole moments, thus to a centrosymmetric material, unusable for 2nd order NLO. Therefore different strategies, using theoretical modeling and fine chemical synthesis were developed. One of them was a successful synthesis of molecules with vanishing ground state dipole moment, i.e. 3-methyl-4-nitropyridine-1-oxyde (POM) [1,2]. Another approach was the synthesis of Λ (or V) type molecules, which because of their structure crystallize in a noncentrosymmetric crystallographic cell [3].The powder data have shown that this is indeed the case. Recently using molecular beam epitaxy (MBE) thin film deposition technique Favaretto et al. [4] obtained noncentrosymmetric thin films with a large second order NLO response.

There exists a class of materials which are *par excellence* noncentrosymmetric. These are chiral materials. Already in seventies/beginning of eighties Zyss et al. [5] as well as Garito [6,7] and coworkers used asymetric carbon atom to incorporate into NLO molecules in order to provide them noncentrosymmetry and as consequence assure growth of noncentrosymmetric crystals. The interest for chiral molecules was shown also by A. Persoons and coworkers [8,9], which provided a theoretical description of the origin of NLO response in these molecules, particularly the magnetic components of susceptibility and elaborated an experimental technique for their measurements. Mercier and coworkers reported synthesis and SHG from $Bi(iii)I_5$ Iodobismuthate [10,11]. In particular they have shown a reversible phase transition from asymmetric intochiral structure when increasing temperature. Zyss and coworkers [12] have shown few years ago that some [2.2] paracyclophanes (as space charge transfer molecules) belonged also to these class of chiral molecule are potentially very interesting for 2nd order NLO applications.

[2.2]Paracyclophane (pCp) are known for almost 60 years. As one of the distinctive features of this intriguing molecule one can mention the rigid molecular structure [13] which offers different possibilities for substitution of either aromatic rings or ethano bridges with formation of 3D-architectures with various substitution patterns [14] (Scheme 1). The strained and stacked structure allows one to hold substituents in close proximity and to utilize the interaction between two aromatic “desks” for the charge transfer [15–18]. On



Scheme 1. Distinctive features of [2.2]paracyclophane derivatives.

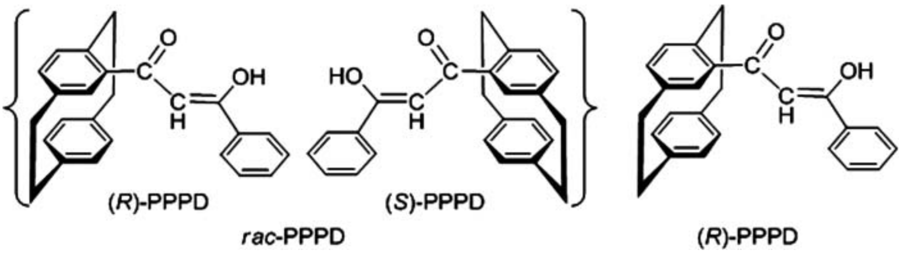


Figure 1. Chemical structures of studied molecules. *Rac*-**1** consists from two enantiomeric forms of *β*-diketone (*R*)-PPPD and (*S*)-PPPDs in equimolar ratio.

the other hand, pCp derivatives could be planar chiral (mono- or polysubstituted in certain positions of aromatic rings), central chiral (substituted in aliphatic CH_2-bridge fragment) or combine in their structure several chiral elements that give rise to a wide range of chiral molecules most of which could be obtained in enantiomerically pure form either by resolution or by synthesis from the respective enantiomerically pure precursors [2,19,20] (Scheme 1). Thus a large number of pCp derivatives can meet the requirements to be noncentrosymmetric and chiral. All this makes this class of compounds very promising for the purposes of nonlinear optical material developments.

In this work we present the preliminary results of our study of linear and nonlinear optical properties of racemic and enantiomerically pure (*R*)-[1-(4-[2.2]paracyclophanyl)]-3-phenylpropane-1,3-diones (*rac*-PPPD and (*R*)-PPPD, Fig. 1) [21], the first representatives of a novel class of noncentrosymmetric molecules, namely planar chiral [2.2]paracyclophane derived *β*-diketones.

2. Experimental Part

Synthesis of β-diketones. All chemicals and solvents were used as purchased without further purification. ^{1}H spectra were recorded on a Bruker AVANCE-400 spectrometer at 400.13 MHz. The residual signals of the solvent protons with the chemical shift δ 7.27 ($CDCl_3$) were used as internal standards. Optical rotation was measured with a Perkin-Elmer-241 polarimeter in a thermostated cell.

Racemic [1-(4-[2.2]paracyclophanyl)]-3-phenylpropane-1,3-dione (*rac*-PPPD) was obtained following the elaborated by us earlier technique which relies on Claisen condensation of racemic 4-acetyl[2.2]paracyclophane **1** with double excess of methylbenzoate **2** in the presence of NaH (60% in oil) in DMSO (Fig. 2) [21]. Enantiomerically pure (*R*)-PPPD was obtained by similar procedure starting from (*R*)-**1** with the chemical yield of 60%. Analytical data are in a good agreement with those obtained for (*S*)-PPPD [21]. (*R*)-PPPD: M. p. 102.5-103.5°C. Found: C 84.90, H 6.34%. $C_{25}H_{22}O_2$ (354.45). Calculated: C 84.72, H 6.26%. $[\alpha]_D{}^{25}$–146 (C 0.6, toluene).

X-ray Analysis. The X-ray analysis was carried out for the single crystal of the racemic PPPD. At 100 K crystals of *rac*-PPPD (C25H22O2, M = 354.43) are orthorhombic, space group Pca21, Z = 4 (Z′ = 1), a = 7.4846(6), b = 11.3092(9), c = 20.7711(16), V = 1758.2(2) Å3, dcalc = 1.339 gcm^{-3}, μ(MoKα) = 0.83 cm^{-1}, F(000) = 752.

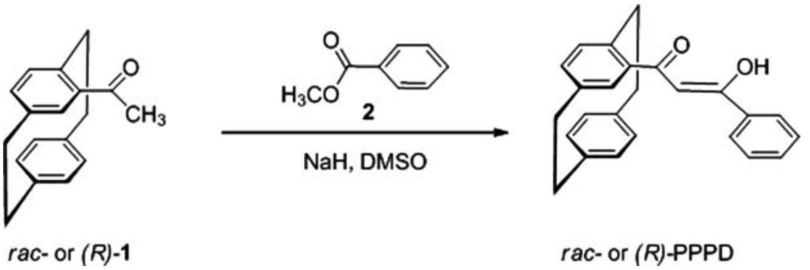


Figure 2. Synthesis of racemic and enantiopure pCp-derived unsymmetrical β-diketones (racemic PPPD and (*R*)-PPPD).

Intensities of 9890 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 58°$] and 2402 independent reflections (Rint = 0.0390) were used in further refinement. Structure was solved by direct method and refined by the full-matrix least-squares technique against F2 in the anisotropic-isotropic approximation. The carbon hydrogen atoms were geometrically positioned and included in refinement using a "riding" model while for hydroxyl group the hydrogen atom was found by the Fourier map syntheses and made rigid. For *rac*-PPPD the refinement converged to wR2 = 0.0955 and GOF = 1.020 for all independent reflections (R1 = 0.0378 was calculated against F for 2192 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0.

Linear Optical Measurements. UV-vis absorption spectra were obtained with Cary 50 Variant spectrophotometr. Steady-state emission and excitation spectra were recorded on Fluorolog FL 3-22 Horiba-Jobin-Yvon photon counting emission spectrometer that is equipped with a 450 W xenon source and double monochromators for excitation and emission. The luminescence spectra observed were corrected for the nonlinear response of the instrument using predetermined factors. Luminescence lifetimes (τ) were measured on samples put into quartz capillaries; they are averages of at least three independent measurements that were achieved by monitoring the decay at the maxima of the emission spectra. The single or bi-exponential decays were analyzed with Origin® 7.0 program.

Powder Second Harmonic Generation Measurements. The second order NLO properties of the two studied molecules were determined by the powder optical second harmonic generation technique, introduced originally by Kurtz and Perry [22]. It is a relatively simple technique which allows a relative comparison of NLO properties of materials, provided that molecules crystallize in a noncentrosymmetric reference frame. Therefore this technique usually doesn't work for charge transfer molecules which, due to the large ground state dipole moments crystallize in tail-head arrangement, thus in a centrosymmetric lattice.

The experimental arrangement used is shown schematically in Fig. 3. The measurements were done using the experiment set up installed newly at Politehnica University of Bucharest, Romania. The infrared light source is a pulsed Q switched Neodymium doped Yttrium Galium laser (Brillant B of Quantel), operating at 1 064.2 nm fundamental wavelength with 5 ns pulse duration and 10 Hz operating rate. Both fundamental and harmonic (532 nm) waves are in the molecule transparency range (cf. Fig. 3). The small amount of powder (30 mg) is pressed between two glass slides and is illuminated with the IR beam with diameter (9 mm) larger than the sample diameter. The SHG intensity

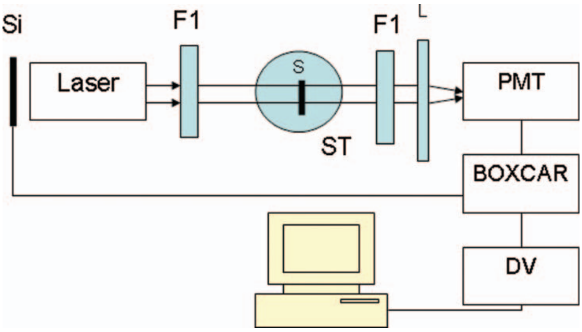


Figure 3. Schematic representation of the experimental set-up for powder second harmonic generation measurements. F1 and F2 are filters, L is focusing lens and DV is digital voltmeter, S is sample and ST is sample stage.

was averaged for a few hundreds of laser pulses. The SHG intensity is calibrated with the similar measurements on a standard, done at the same conditions. As standard the molecule PNP (2-(N-prolinol)-5-nitrypiridyne, characterized for its second order NLO properties by electric field induced optical second harmonic generation (EFISH) and by third harmonic generation (THG) as well as by theoretical calculations by finite-field perturbational approach.23 The use of unfocused large diameter beam allows measuring the SHG intensity from the whole sample volume. It decreases also the light scattering by crystallites.

3. Results and Discussion

3.1. Molecular Structure

According to X-ray diffraction data (XRD), the racemic PPPD crystallizes in noncentrosymmetric space group $Pca2_1$ ($Z = 4$, $R = 0.0361$) that is interesting for the design of molecules appropriate for 2nd order NLO materials. The bond lengths in pCp core are rather close to those observed in isolated pCp (Fig. 4) [24]. At the same time the presence of the β-diketone moiety leads to some elongation of the C(4)-C(5) bond (1.401(3) Å) in comparison with those in the unsubtituted ring (av. 1.392 Å of pCp ring). Both rings are characterized by the boat conformation with the deviation of C(3), C(6) and C(11), C(14) atoms by 0.14 and 0.18 Å, respectively. The twist angle (pseudotorsion angle C(1)-C(2)-C(9)-C(10)) is equal to 9.9°.

In its turn, the bond length distribution and the strength of the intramolecular H-bond are almost identical to those in dibenzoylmethane [25]. The hydrogen bond is asymmetric with H(2O) atom located in the vicinity of O(2) attached to the phenyl ring. The $O(1)\cdots O(2)$ separation, which can serve as a measure of the $O{-}H\cdots O$ bonds strength in PPPD and dibenzoylmethan is 2.449(2) and 2.460(2)Å, respectively.

Analysis of crystal packing (Fig. 5) has revealed that all intermolecular contacts such as $H\cdots H$ and $H\cdots C$ correspond to typical van-der-Waals interactions.

3.2. Photophysical Properties

The absorption spectra of β-diketone PPPD in CH_2Cl_2 at 293 K display intense broad band centered at 355 nm ($\varepsilon = 1800\ M^{-1}\cdot cm^{-1}$) (Fig. 6a). It is noteworthy that racemic and

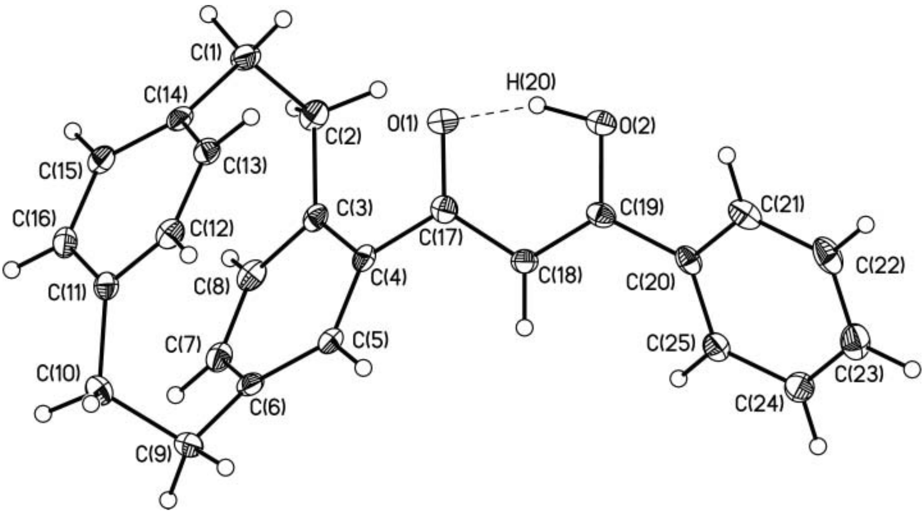


Figure 4. General view of *rac*-PPPD in representation of atoms by thermal motion ellipsoids (p = 50%).

enantiomerically pure samples (*rac*- and (*R*)-PPPD) exhibit practicaly identical absorption spectra. For the isolated moiety pCp (labelled "core") the close proximity of the two benzene rings (3.1 Å) gives rise to abnormal absorption bands that cannot be traced back to the usual $\pi\pi^*$signature of benzene [26]. It exhibits intense, short wavelength absorptions

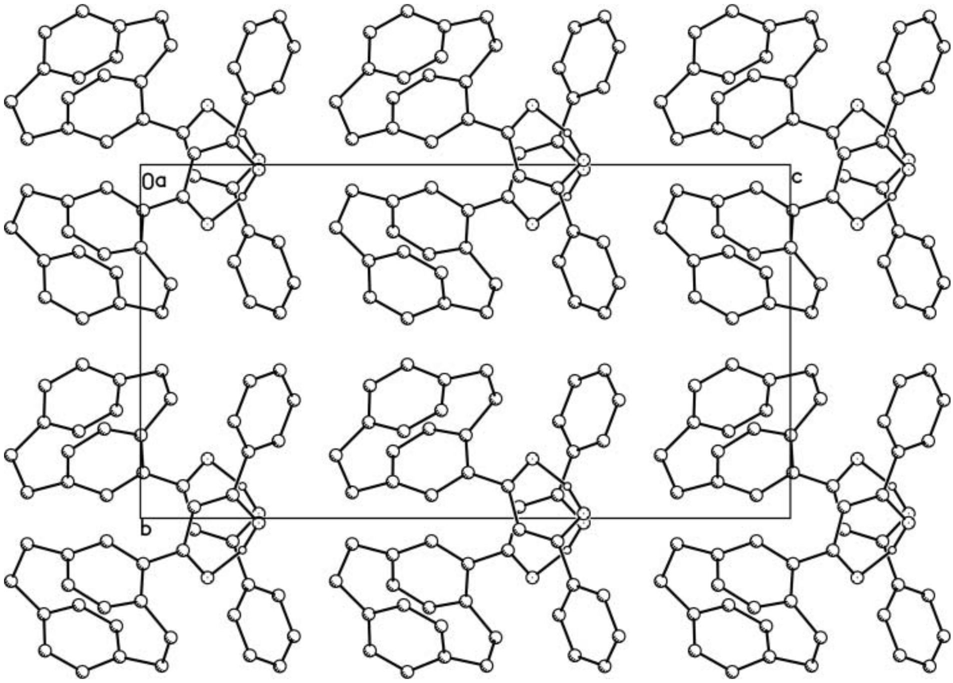


Figure 5. Fragment of crystal packing illustrating the arrangement of molecules along polar axis 2_1.

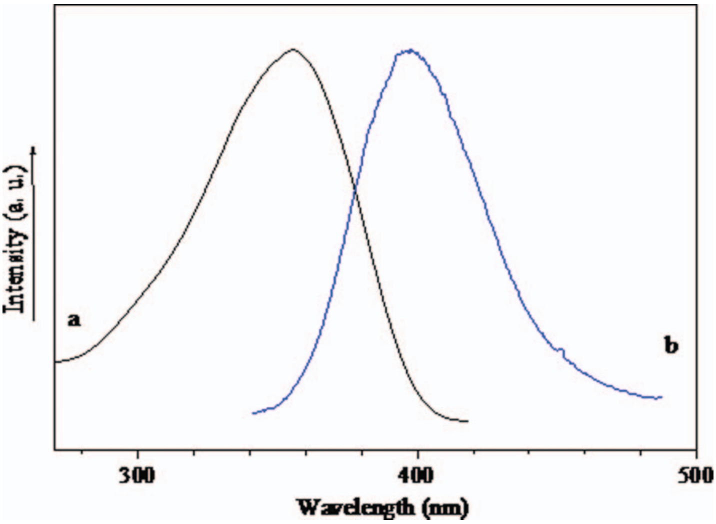


Figure 6. UV-vis absorption (a) and fluorescence emission data (b) for *rac*-PPPD. Emission spectrum was measured by excitation at the absorption maximum.

around 300 nm. These bands are assigned to the π-electron system, which is modified by the loss of planarity and the strong transannular interactions of both benzene rings. So the isolated pCp moiety behaves as a pair of strongly interacting benzene rings and displays spectroscopic features that have been described as analogous to those of a benzene excimer. The attachment of a chromophore (labelled “antenna”) to pCp moiety leads to the changes in the energy of absorption bands. For example, the conjugated isocyanide-containing benzene ring shows the band around 320 nm (respectively, $\varepsilon = 1800\ \mathrm{M^{-1}\cdot cm^{-1}}$ in 2-MeTHF and $\varepsilon = 1900\ \mathrm{M^{-1}\cdot cm^{-1}}$ in PrCN) [27]. In this way the higher energy of $\pi\pi^*$ transition observed for *rac*- and (*R*)-PPPD than one for the isolated pCp is caused by the difference in “antenna”, namely by the presence of the phenyl-substituted β-dicarbonyl fragment. The β-diketone PPPD shows broad emission spectrum with maximum at 400 nm, which is red shifted in comparison with one for the isolated pCp moiety (350 nm) (Fig. 6b). The luminescence excitation spectra for PPPD (*rac*- and (*R*)-PPPD) are quite similar to the absorption spectra.

3.3. Second Order Nonlinear Optical Properties

The results obtained for second order NLO properties are given in Table 1. The $<\chi^{(2)}(-2\omega;\omega,\omega)>$ values are average over all crystallites orientation and nonzero $\chi^{(2)}(-2\omega;\omega,\omega)$ tensor components. From this table one can see that the so averaged quadratic susceptibility of the studied compounds is of the same order of magnitude as that of NPP, being a little smaller.

Both molecules exhibit second harmonic generation ability, the efficiency of which was measured by the powder technique at 1064.2 nm fundamental wavelength and their average NLO susceptibility was found comparable with that of a such well known NLO crystal as PNP.

Table 1. Nonlinear optical properties of [2.2]paracyclophane-derived β-diketones as determeined by powder SHG technique

Compound	SHG intensity (arb. units)	$< \chi^{(2)}(-2\omega; \omega, \omega) >$
PNP	$120 \times 10^{1.2}$ (a)	1(b)
(*R*)-PPPD	180	0.31
rac-PPPD	95	0.22

(a) – correction for used attenuation filter.
(b) – used as standard. Values for studied compounds are relative to PNP.

4. Conclusions

Linear and nonlinear optical properties of two representatives of [2.2]paracyclophane-derived β-diketones, namely racemic and enantiomerically pure (*R*)-[1-(4-[2.2]paracyclo phanyl)]-3-phenylpropane-1,3-diones were investigated for the first time. The data obtained confirm that these compounds crystallize in noncentrosymmetric space group. The relatively low energy of the intense absorption band assigned to the π-electron system (350 nm) in these β-diketones makes them a perspective ligands for a design of coordination compounds for advanced photonic applications able for example to convert a blue light to light of red, green or NIR regions in the case of their complexes with europium, terbium or neodymium ions, respectively. The molecules designed exhibit optical second harmonic generation ability, the efficiency of which was measured by the powder technique at 1064.2 nm fundamental wavelength and their average NLO susceptibility was found comparable with that of such well known NLO crystal as PNP. The zeroth frequency values are expected even to be closer because of larger energy gap of studied compounds as compared with the used standard PNP.

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