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The Use of Structure Analysis Methods in Combination with Semi-empirical Quantum-Chemical Calculations for the Estimation of Quadratic Nonlinear Optical Coefficients of Organic Crystals

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Abstract

An effective search for new organic crystals for prospective use in nonlinear optical (NLO) applications requires quantitative and fast experimental determination of their NLO properties at a molecular level. However, the growth of sufficiently large single crystals, which are needed for structural analysis and refinement by X-ray methods, is a time-consuming and sometimes impossible task. Single crystals of a considerably smaller size may be effectively used for complete structural analysis by electron diffraction combined with simulation methods. When the crystal structure of a given compound is known, its NLO properties may be estimated using quantum-chemical methods for calculation of the molecular nonlinearity tensor and the relationships between its components and the macroscopic coefficients of the crystalline nonlinearity tensor. In the present work, the semiempirical PM-3 method was employed for this aim.

1. Introduction

For the past two decades, the search for organic crystals for nonlinear optical (NLO) applications has been carried out mostly among the π-conjugated systems with effectively one-dimensional charge transfer, having an electron donor substituent at one end and an electron withdrawing one at the other. Following this approach, a number of materials with strong NLO properties has been found (Tomono, Pu, Knoshita, Sasaki & Umegaki, 1993). Usually, the molecular nonlinearities for such systems are rather high. However, for the second-harmonic generation (SHG) process in one-dimensional systems, there exists a fundamental theoretical limit for the coefficient of transformation of the molecular nonlinearity into the crystalline nonlinearity. Depending on the crystal space group and the orientation of the molecules in a crystal cell with respect to the crystal axes, this coefficient may reach a maximum value of 38% at phase matching with respect to the direction of the fundamental beam propagation (Zyss & Oudar, 1982).

Therefore, the search for NLO-active molecules with, at least, two-dimensional intramolecular charge transfer, which would crystallize noncentrosymmetrically, is of both theoretical and practical interest.

It is well known that, for strongly unidimensional systems, the molecular quadratic hyperpolarizability tensor, β_{ijk}, is characterized by a dominant vectorial contribution

$$(\beta)_i = \sum_j \beta_{ijj},$$

where the i axis is parallel to the charge-transfer direction and β_{iii} becomes predominant. In nonlinear molecules, the charge transfer is, at least, two-dimensional in character and the β tensor may contain both the diagonal components β_{iii} as well as off-diagonal ones (Ledoux, Zyss, Siegel, Brienne & Lehn, 1990). In the crystalline state, individual coefficients of the molecular β tensor can be determined provided the crystal structure is known precisely. The relationships between the β_{ijk} values and the crystalline nonlinear tensor coefficients, b_{IJK}, depend on the space group and on the orientation of the molecules in the unit cell with respect to the crystal axes. The details have been explained in a fundamental paper by Zyss & Oudar (1982).

Frequently, it is not possible to grow large single crystals for a full X-ray structure analysis, so that the development of electron crystallography, requiring single crystals that need only be *ca* 100 Å thick and several hundred Å long, becomes mandatary. We have been able to solve several unknown structures using two new methods, namely simulation of electron diffraction patterns from suitable model structures (Voigt-Martin, Schumacher & Garbella, 1992; Voigt-Martin, Yan, Wortmann & Elich, 1995) and maximum entropy combined with log-likelihood statistical calculations (Voigt-Martin, Yan, Gilmore, Shankland & Bricogne, 1994; Voigt-Martin, Yan, Yakimansky, Schollmeyer, Gilmore & Bricogne, 1995).

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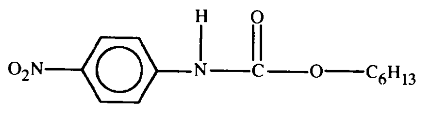
In this paper, the crystal structures of three organic molecules (one one dimensional and two two dimensional) were investigated with the aim of studying the relationship between the properties of molecular polarizability and quadratic hyperpolarizability tensors and the magnitude of the macroscopic NLO effect in one- and two-dimensional systems in the crystalline phase. The two-dimensional molecules studied here belong to the class of bis(benzylidene)ketones. Similar compounds of this class are currently under a thorough investigation as potential candidates for SHG applications (Kawamata, Inoue & Inabe, 1995).

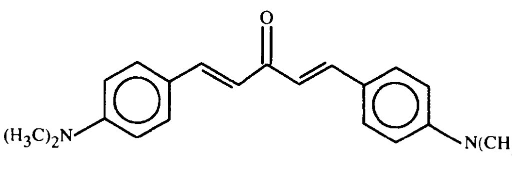
The structural data were used to calculate the angular parameters of the molecular orientations in the cell and to relate the crystalline nonlinear tensor coefficients b_{IJK} to the components of the molecular β tensor. An estimation of the refractive indices of the crystals along the crystal axes and the corresponding local-field factors, relating the b_{IJK} coefficients to the experimentally measurable macroscopic d_{IJK} coefficients, was performed based on the calculated molecular linear polarizability tensor α, reduced to the crystal axes frame. For the calculations of both molecular α and β tensors, the semi-empirical quantum-chemical PM-3 method (Stewart, 1989) was used. Considerably different ratios between the magnitudes of diagonal components of the β tensor β_{iii} and off-diagonal ones were found for the three molecules. Although it is understood that there can be a considerable error in the semi-empirically calculated β-tensor components, the calculations represent a lower limit and indicate that the quadratic susceptibility should be larger than that of urea, in one case, considerably larger. At a qualitative level, this result was fully supported by a SHG experiment.

2. Samples

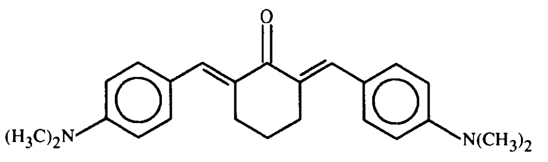
Single crystals of 4-(nitrophenyl)hexylurethane (NPHU) [hexyl (4–nitrophenyl)carbamate] and bis[4-(dimethylamino)benzylidene]acetone (DMABA) were grown from ethanol. Single crystals of 2,6-bis[4-(dimethylamino)benzylidene]cyclohexanone (DMABC) were grown from chloroform.



NPHU



DMABA



DMABC

The colour of the DMABA and DMABC crystals is orange, while NPHU is colourless. Solutions of DMABA and DMABC in dioxane have maximum absorption at wavelengths of λ_m = 427 and 418 nm, respectively.

All the samples indicated strong powder second-harmonic generation efficiencies at a qualitative level (Loos-Wildenauer, Kunz, Voigt-Martin, Yakimanski, Wischerhoff, Zentel, Tschierske & Müller, 1995).

3. Method

Single-crystal electron diffraction data were obtained with a Philips transmission electron microscope, using a rotation-tilt holder in order to obtain diffraction patterns from suitable crystallographic zones. The maximum tilt angle is 60°, so that there is a cone of 30° containing zones inaccessible to electron diffraction. For this reason, X-ray powder diffraction data were used to obtain the supplementary information. For X-ray powder diffraction investigations, a Siemens D-500 diffractometer in the $\Theta/2\Theta$ reflection mode (Cu $K\alpha$ radiation with λ = 1.542 Å) was used.*

For those crystals that were large enough, single-crystal X-ray analysis was used. Data were collected with an Enraf–Nonius Turbo-CAD4 diffractometer in $\omega/2\Theta$ mode (graphite-monochromated Cu $K\alpha$ radiation). The structures were solved by direct methods using *SIR*92 (Giacovazzo, Altomare, Cascarano & Guagliardi, 1992) and refined by full-matrix least-squares analysis using *SHELXL*93 (Sheldrick, 1993). H atoms were refined riding with grouped U's. Experimental details are summarized in Table 1.

The data from electron diffraction and X-ray single-crystal analysis were used to obtain the following information:

(i) crystal class as well as unit-cell parameters;

(ii) the number of molecules per unit cell;

(iii) the space group, indicating the molecular symmetry with respect to the symmetry of the unit cell.

Subsequently, the simulations of the electron diffraction patterns from all zones as well as the X-ray patterns were performed using the *MOPAC*6.0 (Stewart, 1990) and *CERIUS*2.0 molecular simulations programs as described previously (Voigt-Martin, Schumacher

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* The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: AU0077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details for DMABC and NPHU*

	DMABC	NPHU
Crystal data		
Chemical formula	$C_{24}H_{28}N_2O$	$C_{13}H_{18}N_2O_4$
Chemical formula weight	360.48	266.29
Cell setting	Orthorhombic	Monoclinic
Space group	$Cmc2_1$	$P2_1$
a (Å)	21.8575 (9)	5.607 (1)
b (Å)	9.315 (1)	5.756 (1)
c (Å)	9.6437 (6)	21.487 (4)
β (°)		96.94 (1)
V (Å^3)	1963.5 (3)	688.4 (2)
Z	4	2
D_x (Mg m^{-3})	1.219	1.285
Radiation type	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418
No. of reflections for cell parameters	50	41
θ range (°)	23.3–45.3	55.1–71.4
μ (mm^{-1})	0.576	0.797
Temperature (K)	298 (2)	296 (2)
Crystal form	Needle	Long needle
Crystal size (mm)	0.19 × 0.06 × 0.03	1.47 × 0.22 × 0.13
Crystal colour	Light orange	Clear, colourless
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None
No. of measured reflections	1958	3049
No. of independent reflections	1958	2760
No. of observed reflections	1186	2063
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	–	0.0278
$\theta_{\max}$ (°)	74.75	74.69
Range of h, k, l	$0 \rightarrow h \rightarrow 27$ $0 \rightarrow k \rightarrow 11$ $-10 \rightarrow l \rightarrow 12$	$-7 \rightarrow h \rightarrow 7$ $-7 \rightarrow k \rightarrow 6$ $-26 \rightarrow l \rightarrow 26$
No. of standard reflections	3	3
Frequency of standard reflections (min)	66.7	66.7
Intensity decay (%)	5	7
Refinement		
Refinement on	F^2	F^2
R	0.0675	0.0432
wR	0.2067	0.1309
S	1.048	1.054
No. of reflections used in refinement	1958	2752
No. of parameters used	130	185
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0894P)^2 + 2.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.1068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	−0.008	0.000
$\Delta\rho_{\max}$ (e Å^{-3})	0.151	0.126
$\Delta\rho_{\min}$ (e Å^{-3})	−0.205	−0.110
Extinction method	None	*SHELXL*
Extinction coefficient		0.0067 (11)
Source of atomic scattering factors	*International Tables for Crystallography* (1995)	*International Tables for Crystallography* (1995)
Computer programs		
Data collection	*CAD*-4 Enraf–Nonius (1989) software	*CAD*-4 Enraf–Nonius (1989) software
Cell refinement	*CELSIUS* (Svenson, 1974)	*CELSIUS* (Svenson, 1974)
Data reduction	*CORINC* (Dräger & Gattow, 1971; Wiehl & Schollmeyer, 1994)	*CORINC* (Dräger & Gattow, 1971; Wiehl & Schollmeyer, 1994)
Structure solution	*SIR*92 (Giacovazzo *et al.*, 1992)	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

& Garbella, 1992; Voigt-Martin, Yan, Wortmann & Elich, 1995; Voigt-Martin, Yan, Gilmore, Shankland & Bricogne, 1994; Voigt-Martin, Yan, Yakimansky, Schollmeyer, Gilmore & Bricogne, 1995). From these results, model structures were obtained, giving details about the molecular conformation and arrangement in the unit cell. The hyperpolarizability tensor components for the molecules in the unit cells were calculated by the semiempirical PM-3 method (Stewart, 1989) implemented into the *MOPAC* program.

4. Results

4.1. *Crystal structure data*

4.1.1. *NPHU.* These crystals were sufficiently large for X-ray structure determination. The atomic labelling scheme is shown in Fig. 1. The basic projections of the crystal structure are presented in Fig. 2. The relationship between the unit cell and the macroscopic morphology is indicated for the benefit of those undertaking detailed measurements of nonlinear optical susceptibility. The nonlinearity tensor components with respect to molecular orientation are then required.

The space group is $P2_1$ (class 2) and the cell parameters are: $a = 5.607$, $b = 5.756$, $c = 21.487$ Å, $\beta = 96.94°$. There are two molecules per unit cell. The calculated density is $1.285\,\mathrm{g\,cm^{-3}}$. Fractional coordinates and equivalent isotropic thermal parameters are given in Table 2.

4.1.2. *DMABA.*

(*a*) *Experimental electron diffraction patterns*

In this case, the crystals were too small for X-ray structure determination. The electron diffraction patterns from the DMABA single crystals grown from ethanol are shown in Figs. 3–5. The basic [001] zone (Fig. 3) has a net angle of 90° and *d* spacings of the 100 and 010 reflections equal to 6.05 and 7.50 Å much weaker than the even ones, which indicates that they are probably caused by dynamical or secondary scattering and should be extinct. The absence of any other extinctions in the basic zone implies the existence of a twofold screw axis along the *b* axis of the crystal.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (*Å*^{2}) *for NPHU*

$$U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U^{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.3211 (3)	0.2938 (4)	0.41731 (10)	0.0848 (7)
O2	0.6504 (3)	0.3203 (4)	0.47918 (10)	0.0765 (6)
N3	0.5248 (4)	0.2244 (4)	0.43665 (11)	0.0623 (6)
C4	0.6163 (4)	0.0210 (5)	0.40701 (12)	0.0566 (6)
C5	0.4830 (4)	−0.0787 (5)	0.35613 (13)	0.0665 (7)
C6	0.5682 (4)	−0.2713 (5)	0.32839 (13)	0.0668 (7)
C7	0.7905 (4)	−0.3643 (5)	0.35158 (12)	0.0570 (6)
C8	0.9222 (4)	−0.2609 (5)	0.40324 (12)	0.0612 (7)
C9	0.8372 (4)	−0.0690 (5)	0.43130 (12)	0.0596 (6)
N10	0.8911 (4)	−0.5593 (4)	0.32560 (10)	0.0658 (6)
C11	0.8011 (5)	−0.6751 (6)	0.27276 (13)	0.0687 (7)
O12	0.6186 (4)	−0.6332 (5)	0.24018 (11)	0.1068 (9)
O13	0.9514 (3)	−0.8467 (4)	0.26143 (9)	0.0745 (6)
C14	0.8796 (6)	−0.9782 (7)	0.20478 (14)	0.0809 (9)
C15	1.0771 (5)	−1.1383 (6)	0.19370 (14)	0.0782 (9)
C16	1.0218 (6)	−1.2757 (6)	0.13347 (15)	0.0805 (9)
C17	1.2231 (6)	−1.4361 (7)	0.1210 (2)	0.0876 (10)
C18	1.1775 (7)	−1.5780 (7)	0.0624 (2)	0.0960 (11)
C19	1.3779 (7)	−1.7431 (8)	0.0528 (2)	0.1093 (13)

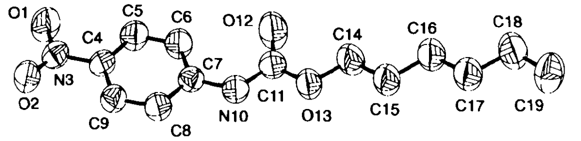


Fig. 1. Molecular structure of 4-nitrophenylhexylurethane (NPHU). Labels of atoms as given in Table 2. *ORTEP* (Johnson, 1976) drawing (thermal ellipsoids at the 50% probability level) without H atoms for better clarity.

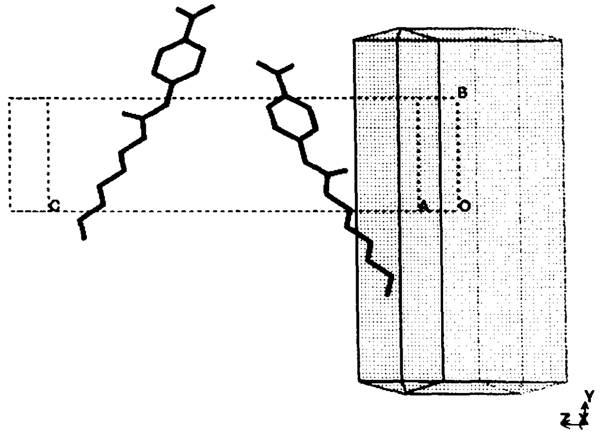


Fig. 2. Crystal structure and morphology of NPHU as determined by X-ray single-crystal analysis. H atoms are omitted for clarity.

Upon tilting the crystal around the a^* axis (Fig. 4) and b^* axis (Fig. 5), no additional extinctions were found. As seen from Fig. 4, tilting around the a^* axis results in an obvious deviation of the net angle from 90°, the diffraction patterns obtained at the tilt angles $+\varphi$ and $-\varphi$ being mirror images of each other. Upon tilting around the b^* axis, the net angle remains 90°. This is characteristic of monoclinic space groups. The value of the monoclinic angle β, estimated from this tilting series by the Vainshtein graphical procedure (Vainshtein, 1964), is *ca* 85°. The only possible space group corresponding to this set of data is $P2_1$ with the monoclinic axis *b*.

The value of the third cell dimension, *c*, may be determined from both the tilting series and the X-ray powder diagram shown in Fig. 6. The X-ray powder diagram contains a very weak peak with the *d* spacing of *ca* 19.5 Å and a strong one with a *d* spacing equal to 9.75 Å. This implies that $c = 19.5/\sin 85°$, these two peaks being 001 and 002, respectively. Thus, the estimated cell parameters are: $a = 6.1$, $b = 7.5$, $c = 19.6$ Å, $\beta = 85°$.

From density considerations, there should be two molecules of DMABA in such a unit cell related to each other by the symmetry of the $P2_1$ space group.

(*b*) *Simulations of the crystal structure and diffraction patterns*

The crystal structure of DMABA in the $P2_1$ space group with the initial cell parameters as estimated above and the initial molecular conformation as calculated by the PM-3 method was simulated using the *CERIUS* program. First, the positions of the molecules in the

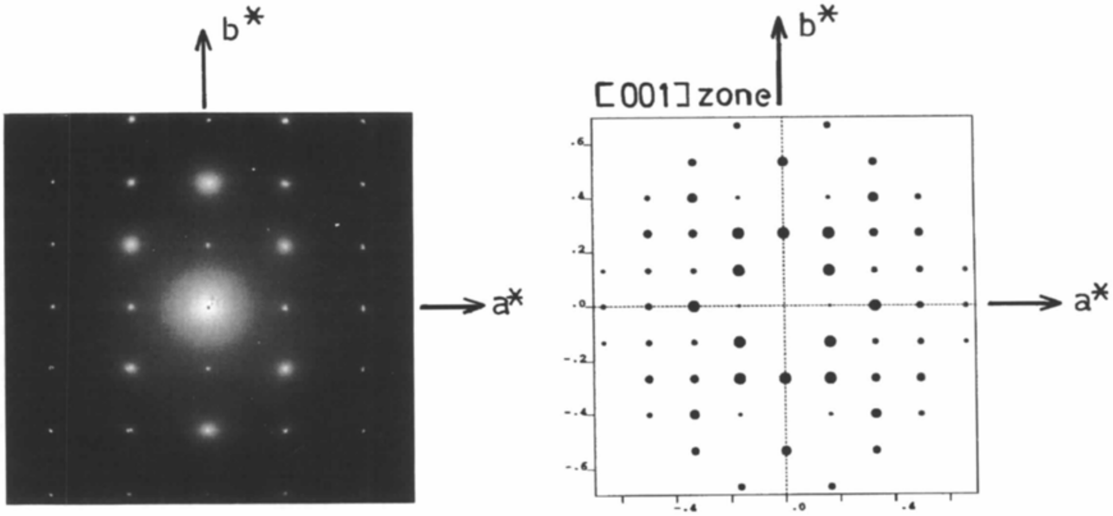
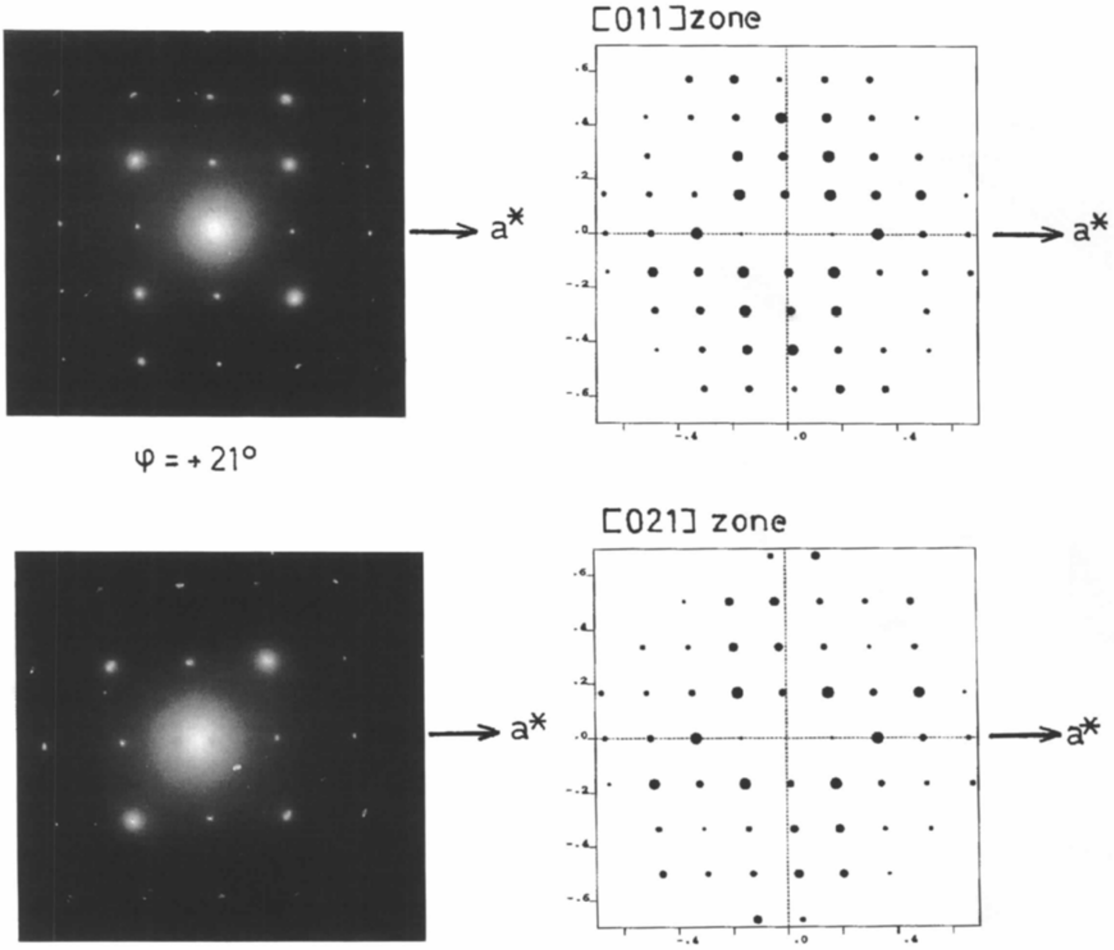


Fig. 3. Experimental and calculated electron diffraction pattern from the basic [001] zone of the DMABA single crystal.



φ = + 21°

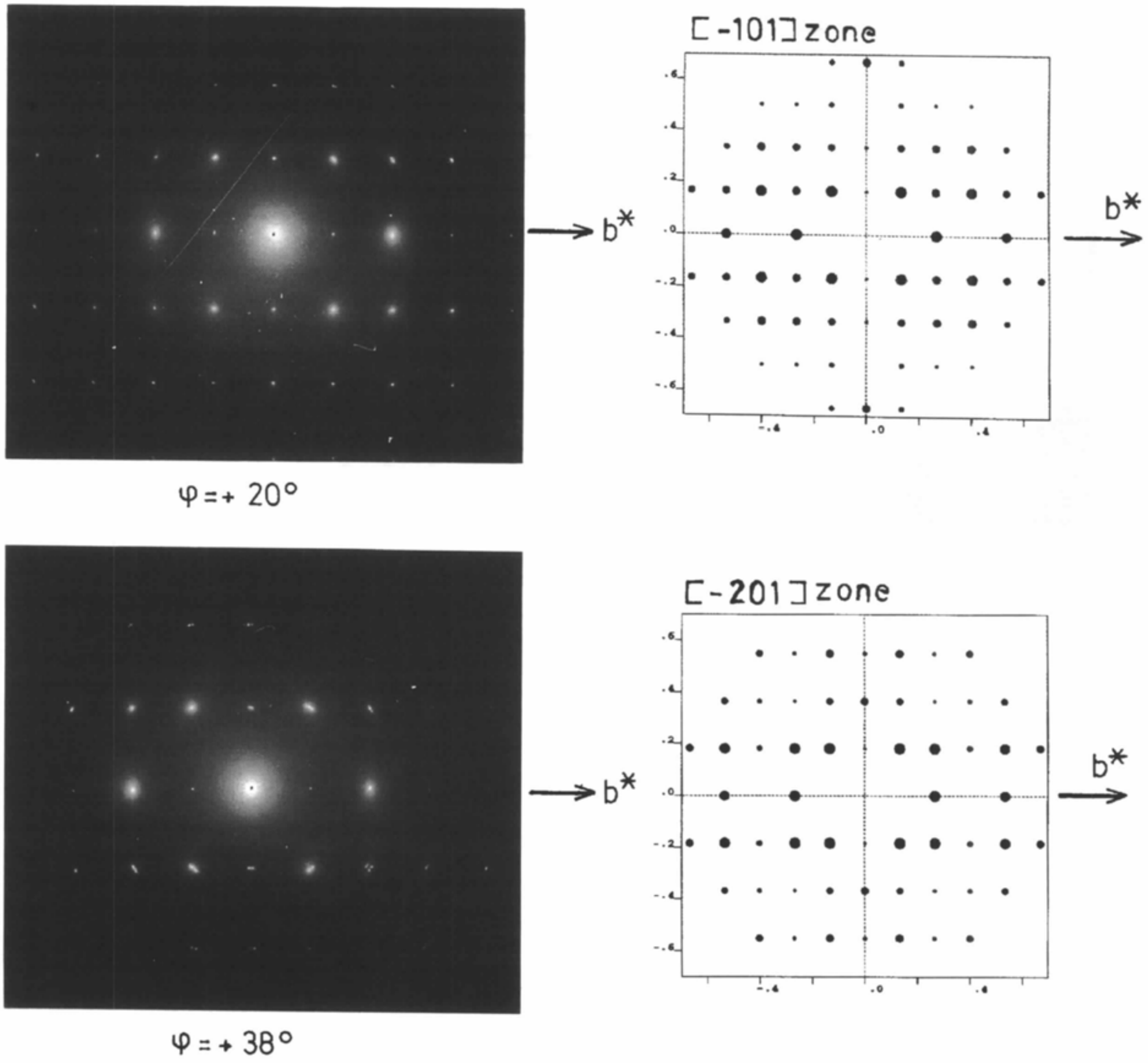
φ = + 38°

Fig. 4. Experimental and calculated electron diffraction patterns obtained from the DMABA single crystal under tilting around the a^* axis (tilt angle is φ).

cell were found which provide an essentially correct reproduction of the most important peaks in the simulated X-ray powder diffraction diagram compared to the experimental one. The cell parameters were adjusted using the Rietveld module available in the *CERIUS*2.0 package. A structure refinement by Rietveld methods was not possible owing to the limited number of reflections. The refined cell parameters are: $a = 6.087$, $b = 7.477$, $c = 19.681$ Å, $\beta = 82.534°$. The calculated density is $1.198\ \mathrm{g\,cm^{-3}}$.

With the refined cell parameters, the crystal packing energy was minimized with respect to the position of the molecule in the cell and its conformation. Fractional coordinates for the resultant structure with an energy of $-46\ \mathrm{kcal\,mol^{-1}}$ per unit cell are given in Table 3 and the labelling scheme is shown in Fig. 7. The final structure together with the morphology are presented in Fig. 8.

The simulated electron diffraction patterns are in very good agreement with the corresponding experimental patterns (see Figs. 3–5). Slight deviations in the calculated relative intensity for the 100 reflection with respect to that of 200 between the simulated and experimental data may be explained by secondary scattering effects resulting in an enhancement of the 100 reflection. As seen from Fig. 6, an agreement between the experimental and simulated X-ray powder diagrams is also quite satisfactory. The most considerable deviation in the intensity is for the 002 reflection at the diffraction angle of 9.06°.



φ = + 20°

φ = + 38°

Fig. 5. Experimental and calculated electron diffraction patterns obtained from the DMABA single crystal under tilting around the b^* axis (tilt angle is φ).

However, it should be noted that DMABA crystals are of plate-like morphology (Fig. 8) and, therefore, have a preferential perpendicular orientation of the crystal *c* axis with respect to the holder surface, resulting in a considerable amplification of measured 00*l* reflections.

In the simulated crystal structure, the molecules are banana shaped and their end-to-end axes lie almost parallel to the *c* axis of the crystal and are shifted along this axis to allow for the most favorable packing of $(H_3C)_2N—C_6H_4$ fragments avoiding the occurrence of chemically equivalent atoms of these fragments in each other's proximities.

The directions of the central C═O bonds of the two molecules in the unit cell are almost perpendicular to the monoclinic *b* axis of the crystal (see Fig. 8). However, the conformation of the molecule is not symmetric with respect to the C═O bond. One of the two C═C bonds lies almost in one plane with the C═O bond, the other is rotated with respect to this plane by *ca* 55°. This conformational feature is in agreement with the data of ^{13}C NMR spectra in the solid state and in chloroform solution: the olefinic C═C carbons give two singlets in solution and two well resolved doublets in the solid state, while the signal of the carbonyl C═O carbon is singlet both in solution and in the solid state.

4.1.3. *DMABC.* Fractional coordinates and equivalent thermal parameters for the crystal structure solved by X-ray single-crystal analysis are given in Table 4 with labelling according to Fig. 9. All basic projections and the morphology are presented in Fig. 10. The space group is $Cmc2_1$ (class *mm*2) and the cell parameters are $a = 21.8575$, $b = 9.315$, $c = 9.6437$ Å. There are four molecules in the unit cell occupying special positions, the mirror plane of the molecule passing through the central C═O bond perpendicular to the molecular axis coincides with the crystal mirror plane. The calculated density is $1.219\,\mathrm{g\,cm^{-3}}$.

4.2. *MOPAC calculations of the molecular polarizabilities in the unit cells and the relationships to macroscopic nonlinear optical coefficients of single crystals*

In this section, macroscopic NLO coefficients, d_{IJK}, are estimated using the PM-3-calculated values of molecular tensor components of linear polarizability and quadratic polarizability:

$$d_{IJK} = (N/V) f_I f_J f_K b_{IJK} = (N/V) f_I f_J f_K \sum c_{xyz}(I,J,K)\beta_{xyz}, \qquad (1)$$

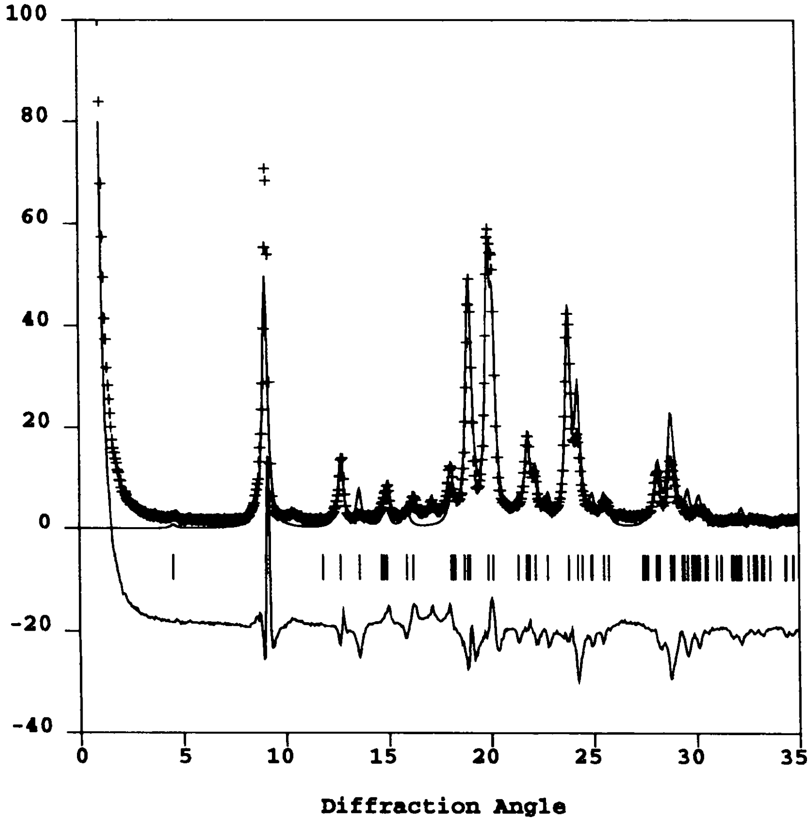


Fig. 6. Experimental (crosses) and simulated (solid line) X-ray powder diffraction diagrams for the DMABA crystals (simulated spectrum is for crystallite sizes of 300 Å in *a*, *b* and *c* directions). The difference spectrum is given at the bottom.

Table 3. *Fractional atomic coordinates for DMABA*

	x	y	z
O	−0.30995	0.53542	0.22626
C1	−0.10908	0.51765	0.22217
C2	0.02417	0.49441	0.15686
C5	0.02590	0.61302	0.10636
C6	0.15778	0.58868	0.04219
C7	0.06767	0.63106	−0.01820
C8	0.19036	0.60822	−0.07966
C9	0.40733	0.54202	−0.08247
C10	0.49778	0.50035	−0.02174
C11	0.37414	0.52357	0.03952
N12	0.54117	0.53173	−0.14596
C13	0.54410	0.35813	−0.18158
C14	0.52403	0.68295	−0.19306
C2*A*	0.01771	0.50924	0.28233
C5*A*	−0.07547	0.47344	0.34450
C6*A*	0.05116	0.46546	0.40342
C7*A*	−0.03881	0.53455	0.46515
C8*A*	0.07885	0.52760	0.52170
C9*A*	0.29046	0.45094	0.51812
C10*A*	0.38082	0.38241	0.45604
C11*A*	0.26223	0.38992	0.39971
N12*A*	0.42014	0.45650	0.57556
C13*A*	0.56699	0.30215	0.58421
C14*A*	0.30403	0.51397	0.64054

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for DMABC*

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	−1/2	−0.2819 (7)	−0.1340 (6)	0.066 (2)
C1	−1/2	−0.3280 (9)	−0.2551 (8)	0.049 (2)
C2	−0.4411 (2)	−0.3582 (6)	−0.3265 (5)	0.0439 (12)
C3	−0.4434 (2)	−0.3985 (7)	−0.4781 (6)	0.0519 (14)
C4	−1/2	−0.3396 (10)	−0.5486 (7)	0.054 (2)
C5	−0.3892 (2)	−0.3409 (6)	−0.2545 (5)	0.0484 (13)
C6	−0.3253 (2)	−0.3615 (6)	−0.2953 (5)	0.0471 (13)
C7	−0.2804 (2)	−0.2877 (7)	−0.2186 (5)	0.056 (2)
C8	−0.2195 (2)	−0.2944 (6)	−0.2529 (6)	0.0550 (15)
C9	−0.1990 (2)	−0.3752 (6)	−0.3639 (5)	0.0492 (14)
C10	−0.2429 (2)	−0.4588 (6)	−0.4344 (6)	0.055 (2)
C11	−0.3043 (2)	−0.4479 (6)	−0.4023 (6)	0.0534 (13)
N12	−0.1380 (2)	−0.3780 (5)	−0.4050 (6)	0.0642 (13)
C13	−0.0931 (2)	−0.2976 (8)	−0.3280 (7)	0.073 (2)
C14	−0.1156 (3)	−0.4879 (8)	−0.4963 (8)	0.083 (2)

where I, J, K are the crystal axes, N is the number of symmetrically related molecules in the unit cell of volume V, b_{IJK} is the unit-cell macroscopic hyperpolarizability per molecule calculated as linear combinations of the molecular hyperpolarizability tensor components β_{xyz} with the coefficients $c_{xyz}(I, J, K)$ derived for different crystal classes (Zyss & Oudar, 1982).

Using the Lorenz–Lorentz relations

$$(n_I^2 - 1)/(n_I^2 + 2) = (4/3)\pi(N/V)\alpha_{II}, \qquad (2)$$

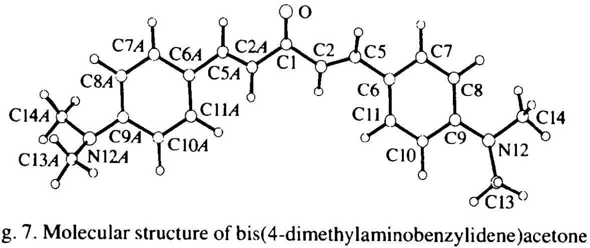


Fig. 7. Molecular structure of bis(4-dimethylaminobenzylidene)acetone (DMABA). Labels of atoms as given in Table 3. *PLUTO* drawing without H atoms for better clarity.

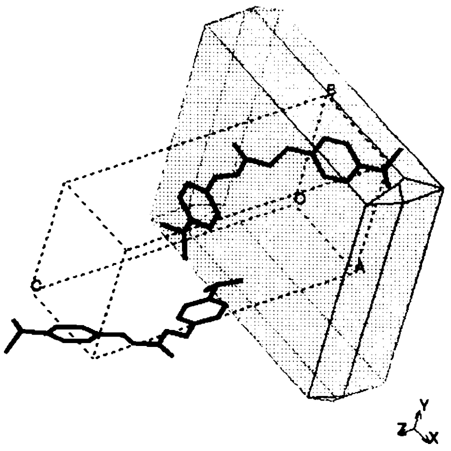


Fig. 8. Crystal structure and morphology of DMABA as determined by the electron diffraction method. H atoms are omitted for clarity.

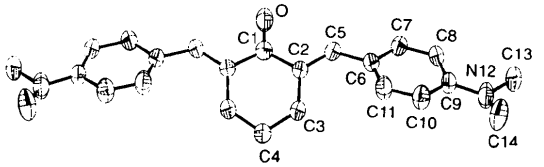


Fig. 9. Molecular structure of 2,6-bis[4-(dimethylamino)benzylidene]-cyclohexanone (DMABC). Labels of atoms as given in Table 4. *ORTEP* drawing (thermal ellipsoids at the 50% probability level) without H atoms for better clarity.

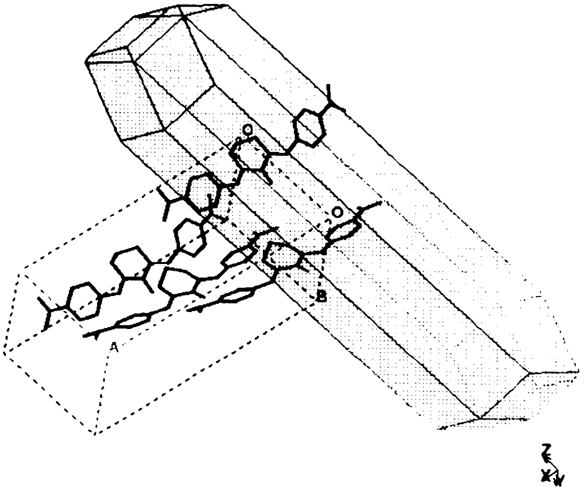


Fig. 10. Crystal structure and morphology of DMABC as determined by X-ray single crystal analysis. H atoms are omitted for clarity.

the local-field factors, f_I, are

$$f_I = (n_I^2 + 2)/3 = 1/[1 - (4/3)\pi(N/V)\alpha_{II}], \qquad (3)$$

where α_{II} are the diagonal components of the α tensor of the unit cell per molecule.

The α_{IJ} values for all the crystals under consideration were estimated using the following approach. The α tensor for a symmetrically independent molecule in a unit cell was calculated by the PM-3 method in the molecular Cartesian coordinate system and then transformed into the coordinate system related to the crystal axes. The rotation matrix of this transformation is determined by the orientation of the molecular axes with respect to the crystal ones and can be easily calculated provided the crystal structure is known. Then the components of the α tensor of the unit cell per molecule are calculated by taking into account the crystal symmetry. For an orthorhombic crystal, the summation of molecular α tensors over all molecules in a unit cell and subsequent dividing by N leads to a cancellation of all off-diagonal components of the α tensor of the unit cell per molecule and leaves the diagonal components unchanged. For a monoclinic crystal with the Y axis parallel to the monoclinic axis, this procedure cancels the α_{XY} and α_{YZ} off-diagonal elements of the α tensor of the unit cell per molecule and retains all diagonal components and the XZ off-diagonal component. The α_{IJ} components of the resultant α tensors of the unit cell per molecule calculated in this way for all the crystals studied are summarized in Table 5. This table also contains the local-field factors, f_I, and refractive indices, n_I, of the crystals calculated from the estimated α_{II} values according to (3).

It seems reasonable to consider here the accuracy of such semiempirical calculations, which should be kept in mind when comparing the calculated and experimentally measured NLO coefficients. Let ΔF and $\delta F = \Delta F/F$ be the absolute and relative errors in a function F, respectively. Then d_{IJK} can be estimated as

$$\begin{aligned}\Delta d_{IJK} = {} & (N/V)b_{IJK}[(\partial f_I/\partial\alpha_{II})f_J f_K \Delta\alpha_{II} \\ & + (\partial f_J/\partial\alpha_{JJ})f_I f_K \Delta\alpha_{JJ} \\ & + (\partial f_K/\partial\alpha_{KK})f_I f_J \Delta\alpha_{KK}] \\ & + (N/V)f_I f_J f_K \textstyle\sum c_{xyz}(I,J,K)\Delta\beta_{xyz}. \qquad (4)\end{aligned}$$

Assuming that, for all I, $\Delta\alpha_{II} = \delta\alpha\alpha_{II}$ and, for all x, y, z, $\Delta\beta_{xyz} = \delta\beta\beta_{xyz}$ and dividing (4) by (1) leads to

$$\begin{aligned}\delta d_{IJK} = {} & \delta\alpha[(\partial \ln f_I/\partial\alpha_{II})\alpha_{II} + (\partial \ln f_J/\partial\alpha_{JJ})\alpha_{JJ} \\ & + (\partial \ln f_K/\partial\alpha_{KK})\alpha_{KK}] + \delta\beta. \qquad (5)\end{aligned}$$

It is easy to see from (3) that $(\partial \ln f_I/\partial\alpha_{II})\alpha_{II} = f_I - 1$ and (5) then transforms into

$$\delta d_{IJK} = \delta\alpha(f_I + f_J + f_K - 3) + \delta\beta. \qquad (6)$$

Table 5. *The PM-3 values of the components of the α tensor of a unit cell per molecule, local-field factors, f_I, and refractive indices, n_I, calculated in the crystal coordinate systems*

	NPHU	DMABA	DMABC	BBCP*
α_{XX} (Å^2)	15.7	28.6	66.0	23.5
α_{YY} (Å^2)	21.5	14.3	15.5	29.5
α_{ZZ} (Å^2)	18.2	50.7	22.3	22.0
α_{XZ} (Å^2)	1.0	−0.7	0	0
f_X	1.236	1.369	2.298	1.389
f_Y	1.354	1.156	1.153	1.542
f_Z	1.284	1.917	1.236	1.355
n_X	1.307	1.452	2.212	1.472 (1.471)
n_Y	1.436	1.212	1.208	1.621 (1.762)
n_Z	1.361	1.963	1.307	1.437 (1.738)

* The values of the refractive indices measured at 1064 nm are given in parentheses (Kawamata, Inoue & Inabe, 1995).

The relative accuracy $\delta\alpha$ of the semiempirically calculated α values may be estimated from a comparison of the calculated and experimental data for benzene [10.14 and 10.33 Å^3, respectively (Kurtz, Stewart & Dieter, 1990)] as acceptable. The comparison of PM-3-calculated α values for polyenes $H(CH{=}CH)_nH$ (n = 2–8) with the *ab initio* values calculated in an extended basis set 6-31G augmented with polarization and diffused basis functions (Kurtz, 1990) gives a $\delta\alpha$ value of less than 10%. As the $(f_I + f_J + f_K - 3)$ value is usually less than 2, the second term dominates in (6) because the semiempirical $\delta\beta$ values may reach 100%, especially for molecules containing nitrophenyl groups (Kurtz, Stewart & Dieter, 1990). Therefore, the value δd_{IJK} = 100% is an estimation of the relative accuracy of PM-3-calculated d_{IJK} values in the worst case (for the whole variety of molecular structures). However, as will be seen in the following, the PM-3 method gives rather good results for the crystal of 2,5-bis(benzylidene)cyclopentanone, which is chemically similar to the DMABA and DMABC molecules.

4.2.1. *NPHU. Nonlinear optical properties.* Since the molecule has essentially a linear extended conformation in the unit cell, the one-dimensional model (Zyss & Oudar, 1982) can be used for the calculation of crystalline nonlinear tensor coefficients, b_{IJK}.

The only molecular nonlinear tensor coefficient, which is necessary for the calculations within the one-dimensional model, is β_{yyy}, where the y direction is along the long axis of the molecule. According to the MOPAC calculation data, $\beta_{yyy} = 8.2 \times 10^{30}$ e.s.u. All other components of the molecular β tensor, as provided by MOPAC, are at least one order of magnitude smaller, confirming the validity of the one-dimensional model.

The only angular parameter, which is needed for calculation in the $P2_1$ space group (class 2), is the angle between the long axis of the molecule and the screw b axis of the crystal (Y axis of the crystal frame). From the crystal structure shown in Fig. 2, this was calculated to be θ = 41.17°.

There are only two nonzero coefficients of the crystalline nonlinear tensor for space groups 2 within the one-dimensional model (Zyss & Oudar, 1982):

$$b_{YYY} = \beta_{yyy}\cos^3\theta, \quad b_{YZZ} = \beta_{yyy}\cos\theta\sin^2\theta.$$

From the values for β_{yyy} and θ calculated for the crystal structure, $b_{YYY} = 3.5 \times 10^{-30}$ and $b_{YZZ} = 2.7 \times 10^{-30}$ e.s.u. The calculated θ value is quite close to the optimum one, $\theta_m = 54.74°$ (Zyss & Oudar, 1982) providing phase-matching conditions with respect to the angular coordinates of the molecule in the cell of space group 2. The b_{YYY} coefficient is not relevant for three-wave mixing owing to additional phase-matching conditions with respect to the propagation direction (Ito, Naito & Inaba, 1975). Thus, the only coefficient observable in the SHG experiments is b_{YZZ}. The coefficient $\cos\theta\sin^2\theta$ of the transformation of the molecular nonlinearity into that of the crystal is equal to 0.326, which is close to the maximum value of 0.385 (Zyss & Oudar, 1982) for one-dimensional systems. Using the local-field factors, as estimated above, and considering them to be frequency independent in the first approximation, one finds the calculated d_{YZZ} coefficient:

$$\begin{aligned} d_{YZZ} &= (N/V)f_Y(f_Z)^2 b_{YZZ} \\ &= 18.5 \times 10^{-9}\ \text{e.s.u.} \\ &= 7.7\ \text{pm V}^{-1}, \end{aligned}$$

which may be compared to the value of $d_{XYZ} = 2.3\ \text{pm V}^{-1}$ for urea single crystals measured at the fundamental frequency of 600 nm (Betzler, Hesse & Loose, 1978).

4.2.2. *DMABA. Nonlinear optical properties.* The one-dimensional model is not relevant for this crystal structure because the DMABA molecule is essentially two dimensional and the largest component of its molecular β tensor is β_{yxx} (the molecular frame xyz is determined by the longest molecular axis x, the two-dimensional charge transfer being mostly realized in the molecular xy plane). Therefore, a two-dimensional model, as proposed by Zyss & Oudar (1982), was used for this crystal structure. The longest x axis of the DMABA molecule in the unit cell is almost parallel to the c axis of the crystal (see Fig. 8), *i.e.* to the Z axis of the crystal frame, while it would be along the X axis of the crystal frame according to the axis convention used by Zyss & Oudar (1982).

According to the *MOPAC* calculation, the components of the molecular β tensor necessary for the calculations within the two-dimensional model are

$$\begin{aligned} \beta_{yyy} &= 0.8 \times 10^{-30}\ \text{e.s.u.} \\ \beta_{yxx} &= 5.7 \times 10^{-30}\ \text{e.s.u.} \\ \beta_{xyy} &= -0.6 \times 10^{-30}\ \text{e.s.u.} \end{aligned}$$

The only angular parameter necessary for the calculations for space groups 2 is the angle α between the y axis of the molecular frame and the twofold axis of the crystal (Y axis of the crystal frame). From the crystal structure presented in Fig. 8, $\alpha = 77.1°$. This leads to the following estimation of the b_{IJK} parameters:

Zyss & Oudar	Fig. 8	
b_{YYY}	$= b_{YYY}$	$= \beta_{yyy}\cos^3\alpha = 0.9 \times 10^{-32}$ e.s.u.
b_{YXX}	$= b_{YZZ}$	$= \beta_{yxx}\cos\alpha = 1.3 \times 10^{-30}$ e.s.u.
b_{YZZ}	$= b_{YXX}$	$= \beta_{yyy}\cos\alpha\sin^2\alpha = 0.2 \times 10^{-30}$ e.s.u.
b_{XYZ}	$= b_{XYZ}$	$= -\beta_{xyy}\cos\alpha\sin\alpha = 0.1 \times 10^{-30}$ e.s.u.

Thus, the calculated d_{YZZ} coefficient is

$$\begin{aligned} d_{YZZ} &= (N/V)f_Y(f_Z)^2 b_{YZZ} \\ &= 12.6 \times 10^{-9}\ \text{e.s.u.} \\ &= 5.2\ \text{pm V}^{-1}. \end{aligned}$$

4.2.3. *DMABC. Nonlinear optical properties.* According to the axis convention used by Zyss & Oudar (1982), the DMABC molecule lies in the molecular xy plane forming an angle $\alpha = 27.74°$ with the twofold screw c axis of the crystal (Z axis of the crystal frame, see Fig. 10). The line of intersection of the molecular xy plane by the XY plane of the crystal is parallel to the mirror XZ plane of the crystal, which, according to the convention used by Zyss & Oudar (1982), indicates that the second angular parameter for groups $mm2$ is $\Phi = 0$. The longest x axis of the molecule in the cell is along the X axis of the crystal frame in agreement with the axis convention used by Zyss & Oudar (1982).

The results of the *MOPAC* calculations of the molecular β-tensor components necessary for the calculations within the two-dimensional model are

$$\beta_{yyy} = 0, \quad \beta_{yxx} = 7.5 \times 10^{-30}, \quad \beta_{xyy} = 0\ \text{e.s.u.}$$

This leads to the following results:

$$\begin{aligned} b_{ZZZ} &= \beta_{yyy}\cos^3\alpha = 0 \\ b_{ZYY} &= -\beta_{xyy}(\sin 2\Phi\sin 2\alpha)/2 + \beta_{yxx}\sin^2\Phi\cos\alpha \\ &\quad + \beta_{yyy}\cos^2\Phi\cos\alpha\sin^2\alpha = 0 \\ b_{ZXX} &= \beta_{xyy}(\sin 2\Phi\sin 2\alpha)/2 + \beta_{yxx}\cos^2\Phi\cos\alpha \\ &\quad + \beta_{yyy}\sin^2\Phi\cos\alpha\sin^2\alpha = 6.6 \times 10^{-30}\ \text{e.s.u.} \end{aligned}$$

The calculated d_{ZXX} coefficient is

$$\begin{aligned} d_{ZXX} &= (N/V)f_Z(f_X)^2 b_{ZXX} \\ &= 85.7 \times 10^{-9}\ \text{e.s.u.} \\ &= 35.7\ \text{pm V}^{-1}. \end{aligned}$$

These results show that the packing of DMABC molecules in the crystal is much more favourable with respect to the realization of NLO properties than the crystal packing of urea. While for a urea crystal $b_{XYZ} = 0.5\beta_{yxx}$, for the DMABC crystal structure $b_{ZXX} = 0.87\beta_{yxx}$. It should be noted that, since β_{yxx} enters the expression for b_{ZXX} with the coefficient $\cos^2\Phi\cos\alpha$, the molecular nonlinearity of a molecule of this type might even be completely transformed into the crystalline nonlinearity if a crystal structure with $\Phi = \alpha = 0$ is realized. In our opinion, this is a potentially very important advantage of the two-dimensional molecules similar to DMABC over the one-dimensional systems for which only 38% at maximum of molecular nonlinearity may be transformed into crystalline nonlinearity (Zyss & Oudar, 1982).

It is worthwhile noting that the DMABC crystal may have both dipolar and octopolar contributions to the macroscopic second-order polarizability since it is an *mm*2 medium and the local symmetry of the molecules in the unit cell is close to C_{2v} (Zyss & Ledoux, 1994). The nature of this contribution may be interpreted within the three-state model (ground state, *g*, plus two excited electronic states, *a* and *b*), its magnitude being proportional to the product $\Delta\mu_{ga}\Delta\mu_{ab}\Delta\mu_{bg}$ ($\Delta\mu_{ij}$ is the transition dipole moment between the states *i* and *j*). The relationships between the magnitude of the octopolar contribution and the molecular β-tensor components for the specific cases of special symmetries have been considered in many publications by Zyss. When irradiated by a laser beam perpendicular to the crystal *Z* plane, corresponding to the *XY* plane depicted in Fig. 17 of the original publication by Zyss & Ledoux (1994), the DMABC crystal should exhibit a considerable octopolar NLO effect. The ratio of the magnitude of the octopolar contribution to that of the dipole one for the *mm*2 unit cell of DMABC may be evaluated then as [Zyss & Ledoux, 1994; equation (D15)]

$$\begin{aligned}\rho &= \{(1/3)[(b_{ZZZ} - 3b_{ZXX})^2 + (b_{XXX} - 3b_{XZZ})^2] \\ &\quad \times [(b_{ZZZ} + b_{ZXX})^2 + (b_{XXX} + b_{XZZ})^2]^{-1}\}^{1/2} \\ &= 3^{1/2},\end{aligned}$$

corresponding to the parameter of the anisotropy of the in-plane nonlinearity $u = b_{ZXX}/b_{ZZZ} = \infty$.

To check the reliability of the semi-empirical PM-3 method for the calculations of molecular α and β tensors, the same calculations, as presented above for the NPHU, DMABA and DMABC crystals, were performed for a crystal of 2,5-bis(benzylidene)cyclopentanone (BBCP) whose NLO coefficients were measured by the Maker-fringe method (Kawamata, Inoue & Inabe, 1995). The space group of this crystal is $C222_1$ (class 222), the number of the molecules in the unit cell $Z = 4$ and cell volume $V = 1406.19$ Å^3 (Kawamata, Inoue & Inabe, 1995). It was found from the atomic coordinates determined by X-ray single-crystal analysis (Theocharis, Jones, Thomas, Motevalli & Hursthouse, 1984) that angular parameters for the two-dimensional model (Zyss & Oudar, 1982) are: the angle between the lines of intersection of the *XY* crystal plane by the *xy* planes of symmetrically equivalent molecules, $2\Phi = 0$; the angle between the molecular *xy* plane and twofold screw, the *Z* axis of the crystal, $\alpha = 49.74°$. The longest *x* axis of the molecular frame is perpendicular to the *X* axis of the crystal, while it should be parallel to the *X* axis, according to the axis convention of the two-dimensional model (Zyss & Oudar, 1982). Therefore, in the equation for the only nonzero coefficient, b_{XYZ}, of the crystalline nonlinearity tensor for groups 222, β_{xyy}, β_{xxx} and β_{yxx} should be used instead of β_{yxx}, β_{yyy} and β_{xyy}, respectively. Taking this into account and using the PM-3 calculated value of $\beta_{yxx} = 3.0 \times 10^{-30}$ e.s.u.,

$$\begin{aligned}b_{XYZ} &= \sin 2\Phi \cos\alpha\,(\beta_{xyy} - \beta_{xxx}\sin^2\alpha) \\ &\quad - \beta_{yxx}\cos 2\Phi \sin 2\alpha \\ &= 2.96 \times 10^{-30}\ \text{e.s.u.}\end{aligned}$$

The NLO coefficient d_{XYZ} may be estimated then by the equation (calculated local-field factors are taken from Table 4)

$$\begin{aligned}d_{XYZ} &= (N/V) f_X f_Y f_Z\, b_{XYZ} \\ &= 24.7 \times 10^{-9}\ \text{e.s.u.} \\ &= 10.3\ \text{pm V}^{-1}.\end{aligned}$$

The calculated d_{XYZ} value is in very good agreement with the experimental one of 7 (2) pm V^{-1} (Kawamata, Inoue & Inabe, 1995) and it is *ca* three times lower than the calculated d_{ZXX} coefficient for the DMABC crystal (see above). This means that the experimental value of the d_{ZXX} coefficient for DMABC may be three times higher than the experimental d_{XYZ} coefficient for BBCP, *i.e.* 20–25 pm V^{-1}.

5. Conclusions

We have investigated three molecules that, on the basis of their chemical structure, do not lead one to expect, *a priori*, a good nonlinear second-harmonic response. NPHU has a strong dipole moment along the molecular axis, so that, with two molecules per unit cell, one might expect virtual cancellation. Both DMABA and DMABC appear to be symmetrical so that, with two and four molecules per unit cell, a centrosymmetric space group seems to be likely. In fact, for the structurally rather similar compounds of the same class of bis(benzylidene)ketones, namely 2,6-bis(benzylidene)cyclohexanone and 3,5-bis[4-(dimethylamino)benzylidene]-1-methyl-4-piperidone, centrosymmetric crystal structures have been determined (Jia, Quail, Arora & Dimmock, 1989).

It was possible to show that all the crystal structures determined by the present structural analysis are noncentrosymmetric and molecular axes are oriented quite favourably with respect to the crystal axes for providing a considerable macroscopic NLO response. In spite of the obviously very rough character of the presented semiempirical estimations of the NLO coefficients because of the neglect of the wavelength dispersion of molecular α and β tensors and failure of the PM-3 method to reproduce experimental β values with high accuracy, the calculations indicate, in agreement with the preliminary powder SHG experiments, that quite large NLO effects are to be expected. It should be noted that semiempirically calculated β values and refractive indices are usually lower than the experimental ones. Therefore, the presented estimations of the NLO coefficients may be considered as lower boundary values. Thus, the most promising molecular crystals for the potential use in NLO applications may be recognized before the effort of growing large single crystals is undertaken and a good understanding of the relationship between molecular parameters and physical properties may be achieved.

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