Synthesis and structural study of a novel nonlinear optical material: the tolane derivative ethyl 2-(4-benzyloxyphenylethynyl)-5-nitrobenzene-1-carbamate

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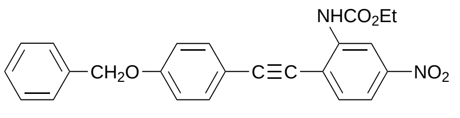
We have synthesized the tolane derivative ethyl 2-(4-benzyloxyphenylethynyl)-5-nitrobenzene-1-carbamate **1**, a promising material for nonlinear optics. Compound **1** has several crystal forms and we have characterized their structural properties by X-ray diffraction. One of the three forms, which is crystallized from a strong polar solvent, has a non-centrosymmetric structure and is *ca.* ten times as strong a second-harmonics generator as *meta*-nitroaniline. A hydrogen bond is found to perform an important role in forming the non-centrosymmetric geometry, which is necessary for a nonlinear optical crystal.

A great deal of work has been performed to make new efficient materials for nonlinear optics. Organic materials are expected to have high nonlinear optical efficiency.[1,2] The large second-order molecular nonlinearity of most organic materials originates from intramolecular charge transfer.[3–5] This interaction is enhanced by donor and acceptor substituents bridged by molecules with a π-electron system.

To achieve efficient nonlinear optical devices, both high hyperpolarizability and an appropriate crystal structure is needed. Although a non-centrosymmetric structure is required for this purpose, molecules with a donor–acceptor system tend to crystallize in a centrosymmetric structure.

Tolane† derivatives are known to have high hyperpolarizability due to the large charge transfer between the two benzene rings bridged by the central triple bond, in spite of a low cut-off wavelength.[6] As is often the case with organic donor–acceptor systems, tolane derivatives also tend to have a centrosymmetric structure and it turns out that the second-order nonlinearity vanishes.[7] More than 150 tolane derivatives have been synthesized and their SHG efficiencies in powder form have been tested by a second-harmonic wave with the evanescent wave (SHEW) technique,[8] some of which have already been reported.[9] Among them we picked out ethyl 2-(4-benzyloxyphenylethynyl)-5-nitrobenzene-1-carbamate **1** (4-nitro-2-ethoxyamido-4′-benzyloxytolane) because it was found to be a promising material during the preliminary investigations. It has a benzyloxy group as a donor and a nitro group as an acceptor. Using differential scanning calorimetry (DSC), we found that **1** has more than two forms of crystal structure. We identified the 2 types of structure by single-crystal X-ray diffraction and discuss here the condition of the appropriate crystal for nonlinear optics.



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Experimental

Synthesis

The synthesis of compound **1** is briefly described. 4-Benzyloxycinnamic acid was prepared by reaction of 4-benzyloxybenzaldehyde, which was prepared from 4-hydroxybenzaldehyde and benzyl bromide with malonic acid.[10] The acid was treated with bromine, followed by elimination of HBr in two steps, which resulted in the formation of 4-benzyloxyphenylacetylene.[11] On the other hand, ethyl 2-bromo-5-nitrobenzene-1-carbamate was prepared by the reaction of 4-bromo-3-amino-nitrobenzene with ethyl chloroformate.[12] Ethyl 2-bromo-5-nitrobenzene-1-carbamate and 4-benzyloxyphenylacetylene were reacted using CuI and $PdCl_2(PPh_3)_2$ in NEt_3 to form ethyl 2-(4-benzyloxyphenylethynyl)-5-nitrobenzene-1-carbamate **1**. The obtained material has a yellow colour. The absorption spectrum of **1** recrystallized from 2-ethoxyethanol is shown in Fig. 1. The cut-off wavelength is 523 nm, which was shortened by the purification.

Differential scanning calorimetry

The thermal analysis was performed with a Perkin-Elmer DSC 7. The cooling and heating rates were 5 °C min^{-1}. After DSC measurement the IR spectrum or the DSC curve of the sample was measured to confirm that the sample had not decomposed.

Crystal structure determination

The single crystals for the X-ray diffraction study were grown in solution by the cooling method. Compound **1** shows polymorphism. As far as we know, compound **1** has three types of crystal structure (designated α, β and γ for simplicity).

To crystallize the α-form crystal, purified **1** was dissolved in 2-ethoxyethanol at 40 °C until the solution was almost satu-

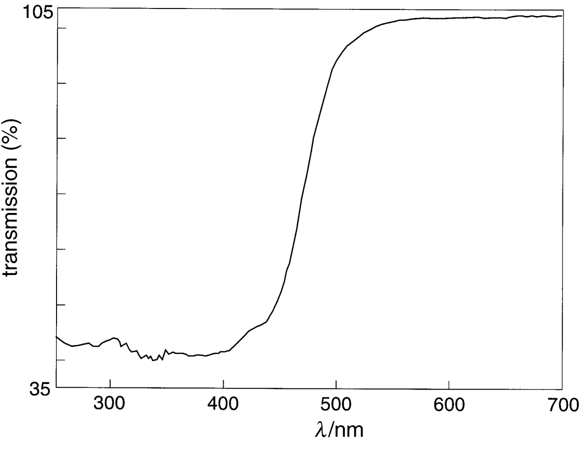

Fig. 1 The absorption spectrum of the α-form crystal

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† IUPAC name: diphenylacetylene.

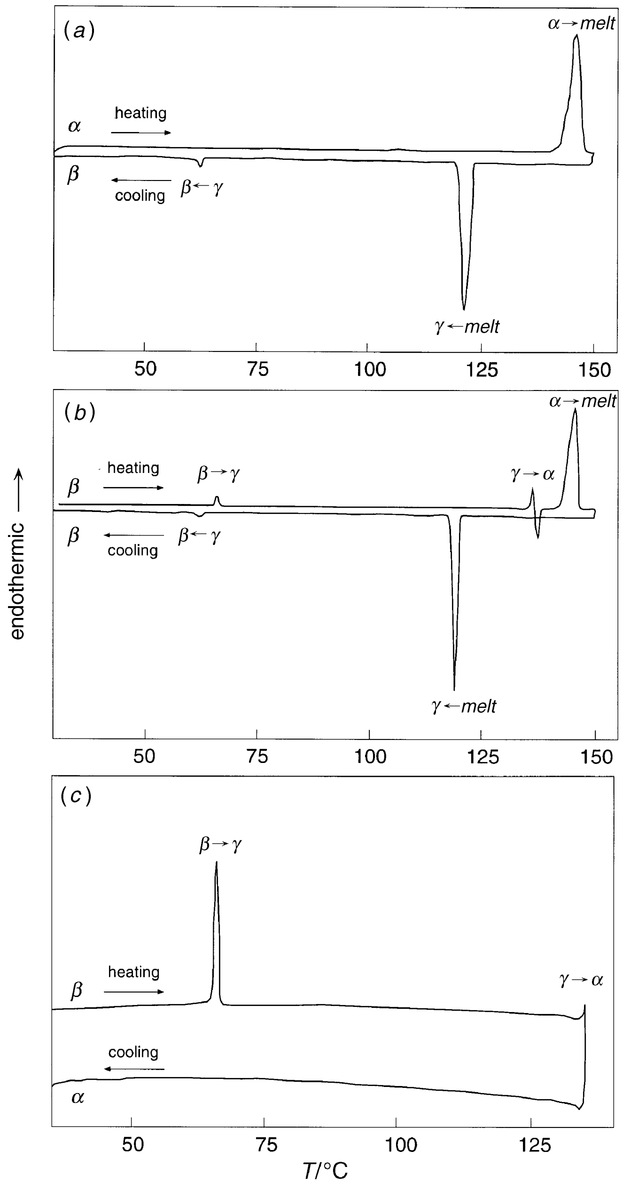

Fig. 2 (*a*) DSC curve of compound **1**. Starting from the α-form crystal, the sample was heated to 150 °C and kept at that temperature for 5 min. Then it was cooled to room temperature. The arrows show the direction of heating and cooling. (*b*) DSC curve starting with the β-form crystal. The sample was kept at 150 °C for 5 min. (*c*) DSC curve starting with the β-form crystal. The sample was kept at 135 °C for 5 min, then cooled down.

Table 1 Crystallographic data α- and β-form crystals

sample name	α-form	β-form
molecular formula	$C_{24}H_{20}N_2O_5$	$C_{24}H_{20}N_2O_5$
molecular weight	416.42	416.42
crystal system	monoclinic	monoclinic
space group	*Cc* (No. 9)	$P2_1/c$ (No. 14)
unit cell dimensions		
a/Å	25.827(5)	10.514(1)
b/Å	4.947(2)	42.385(4)
c/Å	21.089(8)	14.185(2)
β/degrees	127.78(4)	90.47(1)
unit cell volume *U* (Å^3)	2129.5(6)	6321(1)
Z	4	12
D (mg m^{-3})	1.299	1.313
no. of observed reflections	2614	7829
no. of refined parameters	361	1039
R	0.056	0.087
computer and programs	FACOM M-1800, UNICS-III program system	

Table 2 Selected bond lengths of the α-form crystal[a]

bond	length/Å	bond	length/Å
O(17)–C(16)	1.335(0.006)	O(17)–C(18)	1.466(0.009)
O(20)–C(16)	1.188(0.008)	O(22)–N(21)	1.230(0.007)
O(23)–N(21)	1.202(0.011)	O(24)–C(12)	1.371(0.009)
O(24)–C(25)	1.398(0.012)	N(15)–C(3)	1.402(0.006)
N(15)–C(16)	1.359(0.008)	N(15)–H(N15)	0.946(0.057)
N(21)–C(5)	1.440(0.010)	C(1)–C(2)	1.423(0.010)
C(1)–C(8)	1.184(0.010)	C(2)–C(3)	1.426(0.011)
C(2)–C(7)	1.409(0.008)	C(3)–C(4)	1.380(0.010)
C(4)–C(5)	1.395(0.007)	C(5)–C(6)	1.417(0.012)
C(6)–C(7)	1.359(0.011)	C(8)–C(9)	1.443(0.010)
C(9)–C(10)	1.406(0.008)	C(9)–C(14)	1.376(0.013)
C(10)–C(11)	1.376(0.012)	C(11)–C(12)	1.404(0.013)
C(12)–C(13)	1.365(0.008)	C(13)–C(14)	1.397(0.011)
C(18)–C(19)	1.468(0.011)	C(25)–C(26)	1.528(0.010)
C(26)–C(27)	1.375(0.009)	C(26)–C(31)	1.344(0.014)
C(27)–C(28)	1.380(0.012)	C(28)–C(29)	1.359(0.016)
C(29)–C(30)	1.352(0.011)	C(30)–C(31)	1.380(0.011)

[a] E.s.d.s shown in parentheses.

rated and was then cooled slowly at a rate of 0.1–0.2 °C h^{-1}. After the solution had reached room temperature, crystals were picked from the solution and rinsed with a solvent to clean the crystal surfaces. The acquired crystal had a long, narrow shape, with dimensions of approximately 1 × 3 × 0.4 mm. The crystal had partially plane and parallel surfaces. This area was about 1 × 1 mm in size.

To obtain the β-form crystal, the same procedure was performed but ethyl acetate was used as a solvent. The β-form crystals easily formed as a large parallelogram platelet crystal of dimensions 10 × 10 × 1 mm.

The γ-form crystal appears to be unstable, because it only appears during the thermal processes as mentioned in the next section. It was not obtained at room temperature.

Cell parameters and intensity data for the α-form crystals were derived from measurements on a Rigaku AFC-4 four-circle diffractometer and the data for the β-form crystals were from an Enraf-Nonius CAD-4 diffractometer. Molecular and crystal structures were determined by direct methods using MULTAN78, and were refined by use of the block-diagonal least-square method.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/29.

Linear and nonlinear optical measurements

The UV–visible absorption spectra were measured with a HITACHI spectrophotometer U-3400.

The directions of the optical axes of the crystal were defined by the conoscopic figure with the polarizing microscope at a wavelength of 532 nm. The refractive indices were measured by the observation of Becke's line. To fit the Sellmeier equation, measurements at three wavelengths (532, 589 and 633 nm) were performed. All the optical measurements were performed only on the α-form crystals.

Nonlinear optical properties were evaluated using the SHEW technique. Details of this technique are described in ref. 8. The compound was crushed into a fine powder and pushed into contact with a surface of a total reflection prism made of rutile. The fundamental wave of a Q-switched Nd:YAG laser (λ = 1064 nm) was guided into the prism and was totally reflected at the boundary. The reflected second-harmonics (SH) were detected and their power was compared with that of *meta*-nitroaniline (*m*-NA) measured under the same conditions.

Results and Discussion

Differential scanning calorimetry (DSC) analysis shows how the α-, β- and γ-forms appear. Fig. 2(*a*) shows the DSC curve produced when the α-form crystal was heated. The crystal was heated to 150 °C, the temperature maintained for 5 min and then cooled to 30 °C. The α-form crystal melts at 143.1 °C. In the cooling process a small exothermic peak was observed at 63.3 °C after the solidification. Since the final crystal obtained after the entire process proved to be the β-form crystal, this small exothermic peak can be regarded as a phase transition to the β-form crystal. It might be thought that the β-form crystal is transformed from the α-form crystal at 63.3 °C, but the DSC curve in Fig. 2(*b*) shows another explanation.

Fig. 2(*b*) illustrates the heating and cooling processes starting from the β-form crystal. When the β-form crystal was heated, a transition occurred at 65.5 °C which was indicated by a small endothermic peak. Another transition was observed at 135.5 °C and then the crystal melted at the melting point of the α-form crystal; the second transition at 135.5 °C is therefore the transition to the α-form crystal, and thus the first transition must be considered as the transition to another form, which is the γ-form. The IR spectra at 80 °C also showed that the crystal in the intermediate is very different from the α-form crystal, that is, the γ-form crystal. Although the detailed structure of the γ-form has not been investigated as yet, it is expected that it is little different from the β-form crystal because the IR spectrum of the γ-form crystal was similar to that of the β-form crystal. Thus the difference between the β- and γ-forms is probably a small conformational change in the benzyloxy or carbamate substituents, or a different rotational angle around the C≡C axis.

On the other hand, the enthalpy of the smaller exothermic peak at 63.3 °C in the cooling process is equivalent to that of the endothermic peak at 65.4 °C in the heating process. Therefore the crystal formed during cooling from 120.3 to 65.4 °C was also the γ-form crystal. The cooling curve in Fig. 2(*a*) is same as that in Fig. 2(*b*), so that in the cooling process the γ-form always crystallizes from the melted compound 1 and then transforms to the β-form crystal at 65.4 °C.

Fig. 2(*c*) shows the possibility of obtaining the α-form crystals from the β-form crystals. When the β-form crystal was heated until the transition to the α-form at 135.5 °C, and then cooled down before it melted, the α-form remained. The α-form structure was confirmed by IR spectroscopy and an X-ray diffraction pattern. While the newly-formed α-form crystals outwardly maintained the large size of the β-form crystals, the crystals became opaque at the transition, indicating that they were no longer *single* crystals. This is because the structures of the α- and β-form crystals are very different, as mentioned in the following.

Table 3 Selected bond angles of the α-form crystal[a]

bonds	angle (°)	bonds	angle (°)
C(16)–O(17)–C(18)	115.1(0.5)	C(12)–O(24)–C(25)	116.7(0.5)
C(3)–N(15)–C(16)	123.9(0.5)	C(3)–N(15)–H(N15)	124.2(3.1)
C(16)–N(15)–H(N15)	111.9(3.1)	O(22)–N(21)–O(23)	123.0(0.7)
O(22)–N(21)–C(5)	117.5(0.7)	O(23)–N(21)–C(5)	119.6(0.5)
C(2)–C(1)–C(8)	174.4(0.6)	C(1)–C(2)–C(3)	119.7(0.5)
C(1)–C(2)–C(7)	121.5(0.7)	C(3)–C(2)–C(7)	118.8(0.7)
N(15)–C(3)–C(2)	117.0(0.6)	N(15)–C(3)–C(4)	122.2(0.7)
C(2)–C(3)–C(4)	120.8(0.5)	C(3)–C(4)–C(5)	118.3(0.7)
N(21)–C(5)–C(4)	118.4(0.7)	N(21)–C(5)–C(6)	119.4(0.5)
C(4)–C(5)–C(6)	122.2(0.6)	C(5)–C(6)–C(7)	118.7(0.5)
C(2)–C(7)–C(6)	121.3(2.9)	C(1)–C(8)–C(9)	177.0(0.8)
C(8)–C(9)–C(10)	118.6(0.8)	C(8)–C(9)–C(14)	121.2(0.5)
C(10)–C(9)–C(14)	120.2(0.7)	C(9)–C(10)–C(11)	119.8(0.8)
C(10)–C(11)–C(12)	119.7(0.6)	O(24)–C(12)–C(11)	114.8(0.5)
O(24)–C(12)–C(13)	125.0(0.8)	C(11)–C(12)–C(13)	120.2(0.7)
C(12)–C(13)–C(14)	120.5(0.8)	C(9)–C(14)–C(13)	119.5(0.6)
O(17)–C(16)–O(20)	124.6(0.5)	O(17)–C(16)–N(15)	108.9(0.5)
O(20)–C(16)–N(15)	126.4(0.5)	O(17)–C(18)–C(19)	107.1(0.7)
O(24)–C(25)–C(26)	109.7(0.5)	C(25)–C(26)–C(27)	124.1(0.8)
C(25)–C(26)–C(31)	117.8(0.6)	C(27)–C(26)–C(31)	118.2(0.7)
C(26)–C(27)–C(28)	120.2(1.0)	C(27)–C(28)–C(29)	120.3(0.7)
C(28)–C(29)–C(30)	119.7(0.8)	C(29)–C(30)–C(31)	119.5(1.0)
C(26)–C(31)–C(30)	122.1(0.7)		

[a] E.s.d.s shown in parentheses.

Table 4 Selected bond lengths of the β-form crystal[a]

bond	length/Å	bond	length/Å
O(17)A–C(16)A	1.336(0.007)	O(17)A–C(18)A	1.502(0.008)
O(20)A–C(16)A	1.196(0.007)	O(22)A–N(21)A	1.216(0.007)
O(23)A–N(21)A	1.218(0.007)	O(24)A–C(12)A	1.380(0.007)
O(24)A–C(25)A	1.410(0.008)	N(15)A–C(3)A	1.395(0.007)
N(15)A–C(16)A	1.381(0.007)	N(15)A–H(N15)A	0.968(0.054)
N(21)A–C(5)A	1.502(0.007)	C(1)A–C(2)A	1.432(0.008)
C(1)A–C(8)A	1.176(0.008)	C(2)A–C(3)A	1.418(0.008)
C(2)A–C(7)A	1.383(0.008)	C(3)A–C(4)A	1.388(0.008)
C(4)A–C(5)A	1.394(0.008)	C(5)A–C(6)A	1.347(0.008)
C(6)A–C(7)A	1.383(0.008)	C(8)A–C(9)A	1.464(0.008)
C(9)A–C(10)A	1.401(0.009)	C(9)A–C(14)A	1.374(0.008)
C(10)A–C(11)A	1.376(0.009)	C(11)A–C(12)A	1.403(0.009)
C(12)A–C(13)A	1.381(0.009)	C(13)A–C(14)A	1.402(0.008)
C(18)A–C(19)A	1.407(0.010)	C(25)A–C(26)A	1.517(0.008)
C(26)A–C(27)A	1.375(0.009)	C(26)A–C(31)A	1.377(0.009)
C(27)A–C(28)A	1.375(0.009)	C(28)A–C(29)A	1.367(0.011)
C(29)A–C(30)A	1.365(0.010)	C(30)A–C(31)A	1.392(0.009)
O(17)B–C(16)B	1.351(0.007)	O(17)B–C(18)B	1.522(0.008)
O(20)B–C(16)B	1.194(0.007)	O(22)B–N(21)B	1.216(0.007)
O(23)B–N(21)B	1.230(0.006)	O(24)B–C(12)B	1.366(0.007)
O(24)B–C(25)B	1.440(0.007)	N(15)B–C(3)B	1.396(0.007)
N(15)B–C(16)B	1.368(0.007)	N(15)B–H(N15)B	0.934(0.055)
N(21)B–C(5)B	1.500(0.007)	C(1)B–C(2)B	1.431(0.008)
C(1)B–C(8)B	1.186(0.008)	C(2)B–C(3)B	1.416(0.008)
C(2)B–C(7)B	1.403(0.008)	C(3)B–C(4)B	1.381(0.008)
C(4)B–C(5)B	1.386(0.008)	C(5)B–C(6)B	1.370(0.008)
C(6)B–C(7)B	1.381(0.008)	C(8)B–C(9)B	1.462(0.008)
C(9)B–C(10)B	1.392(0.008)	C(9)B–C(14)B	1.391(0.008)
C(10)B–C(11)B	1.364(0.008)	C(11)B–C(12)B	1.380(0.008)
C(12)B–C(13)B	1.401(0.008)	C(13)B–C(14)B	1.398(0.008)
C(18)B–C(19)B	1.284(0.012)	C(25)B–C(26)B	1.513(0.008)
C(26)B–C(27)B	1.357(0.009)	C(26)B–C(31)B	1.400(0.009)
C(27)B–C(28)B	1.386(0.009)	C(28)B–C(29)B	1.348(0.009)
C(29)B–C(30)B	1.375(0.010)	C(30)B–C(31)B	1.396(0.009)
O(17)C–C(16)C	1.357(0.007)	O(17)C–C(18)C	1.526(0.008)
O(20)C–C(16)C	1.213(0.007)	O(22)C–N(21)C	1.226(0.007)
O(23)C–N(21)C	1.224(0.007)	O(24)C–C(12)C	1.368(0.007)
O(24)C–C(25)C	1.435(0.008)	N(15)C–C(3)C	1.387(0.007)
N(15)C–C(16)C	1.341(0.007)	N(15)C–H(N15)C	1.040(0.056)
N(21)C–C(5)C	1.497(0.007)	C(1)C–C(2)C	1.419(0.009)
C(1)C–C(8)C	1.194(0.009)	C(2)C–C(3)C	1.419(0.008)
C(2)C–C(7)C	1.405(0.009)	C(3)C–C(4)C	1.394(0.008)
C(4)C–C(5)C	1.388(0.008)	C(5)C–C(6)C	1.375(0.008)
C(6)C–C(7)C	1.382(0.009)	C(8)C–C(9)C	1.450(0.009)
C(9)C–C(10)C	1.405(0.009)	C(9)C–C(14)C	1.397(0.008)
C(10)C–C(11)C	1.355(0.009)	C(11)C–C(12)C	1.400(0.009)
C(12)C–C(13)C	1.389(0.009)	C(13)C–C(14)C	1.404(0.009)
C(18)C–C(19)C	1.470(0.010)	C(25)C–C(26)C	1.516(0.009)
C(26)C–C(27)C	1.367(0.009)	C(26)C–C(31)C	1.398(0.009)
C(27)C–C(28)C	1.377(0.010)	C(28)C–C(29)C	1.364(0.010)
C(29)C–C(20)C	1.378(0.010)709	C(30)C–C(31)C	1.396(0.009)

[a] E.s.d.s shown in parentheses.

All the obtained parameters of the α- and β-forms of **1** from the X-ray diffraction studies are summarized in Table 1. The selected bond lengths and the angles of the α-form crystals are summarized in Tables 2 and 3, and those of the β-form crystals are in Tables 4 and 5, respectively. The space group of the α-form was determined to be monoclinic *Cc*, which is non-centrosymmetric, while on the other hand, the β-form crystals are centrosymmetric, and therefore not SH active.

For the future study of this potentially SH active material, we characterized the linear optical properties of the α-form

Table 5 Selected bond angles of the β-form crystal[a]

bonds	angle (°)	bond	angle (°)
C(16)A–O(17)A–C(18)A	111.4(0.4)	C(12)A–O(24)A–C(25)A	118.7(0.5)
C(3)A–N(15)A–C(16)A	125.6(0.5)	C(3)A–N(15)A–H(N15)A	120.1(3.23)
C(16)A–N(15)A–H(N15)A	114.1(3.3)	O(22)A–N(21)A–O(23)A	124.5(0.5)
O(22)A–N(21)A–C(5)A	117.2(0.5)	O(23)A–N(21)A–C(5)A	118.4(0.5)
C(2)A–C(1)A–C(8)A	176.7(0.6)	C(1)A–C(2)A–C(3)A	118.5(0.5)
C(1)A–C(2)A–C(7)A	121.0(0.5)	C(3)A–C(2)A–C(7)A	120.5(0.5)
N(15)A–C(3)A–C(2)A	118.1(0.5)	N(15)A–C(3)A–C(4)A	122.7(0.5)
C(2)A–C(3)A–C(4)A	119.3(0.5)	C(3)A–C(4)A–C(5)A	117.0(0.5)
N(21)A–C(5)A–C(4)A	115.3(0.5)	N(21)A–C(5)A–C(6)A	119.8(0.5)
C(4)A–C(5)A–C(6)A	124.9(0.5)	C(5)A–C(6)A–C(7)A	118.2(0.5)
C(2)A–C(7)A–C(6)A	120.2(0.5)	C(1)A–C(8)A–C(9)A	178.9(0.6)
C(8)A–C(9)A–C(10)A	118.3(0.5)	C(8)A–C(9)A–C(14)A	121.1(0.5)
C(10)A–C(9)A–C(14)A	120.5(0.6)	C(9)A–C(10)A–C(11)A	120.0(0.6)
C(10)A–C(11)A–C(12)A	119.0(0.6)	O(24)A–C(12)A–C(11)A	113.8(0.5)
O(24)A–C(12)A–C(13)A	124.8(0.5)	C(11)A–C(12)A–C(13)A	121.4(0.6)
C(12)A–C(13)A–C(14)A	118.7(0.5)	C(9)A–C(14)A–C(13)A	120.2(0.5)
O(17)A–C(16)A–C(20)A	126.0(0.5)	O(17)A–C(16)A–N(15)A	108.2(0.5)
O(20)A–C(16)A–N(15)A	125.9(0.5)	O(17)A–C(18)A–C(19)A	107.1(0.5)
O(24)A–C(25)A–C(26)A	107.5(0.5)	C(25)A–C(26)A–C(27)A	122.4(0.6)
C(25)A–C(26)A–C(31)A	118.3(0.5)	C(27)A–C(26)A–C(31)A	119.3(0.6)
C(26)A–C(27)A–C(28)A	120.3(0.7)	C(27)A–C(28)A–C(29)A	120.6(0.7)
C(28)A–C(29)A–C(30)A	119.6(0.6)	C(29)A–C(30)A–C(31)A	120.4(0.6)
C(26)A–C(31)A–C(30)B	119.8(0.6)	C(12)B–N(24)B–C(25)B	117.0(0.4)
C(16)B–O(17)B–C(18)B	112.6(0.5)	C(3)B–N(15)B–H(N15)B	119.0(0.4)
C(3)B–N(15)B–C(16)B	125.7(0.5)	O(22)B–N(21)B–O(23)B	124.8(0.5)
C(16)B–N(15)B–H(N15)B	115.3(3.4)	O(23)B–C(21)B–C(5)B	118.1(0.5)
O(22)B–N(21)B–C(5)B	117.1(0.5)	C(1)B–C(2)B–C(3)B	120.2(0.5)
C(2)B–C(1)B–C(8)B	179.6(0.6)	C(2)B–C(2)B–C(7)B	119.9(0.5)
C(1)B–C(2)B–C(7)B	119.9(0.5)	N(15)B–C(3)B–C(4)B	123.3(0.5)
N(15)B–C(3)B–C(2)B	117.1(0.5)	C(3)B–C(4)B–C(5)B	117.7(0.5)
C(2)B–C(3)B–C(4)B	119.6(0.5)	N(21)B–C(5)B–C(6)B	118.4(0.5)
N(21)B–C(5)B–C(4)B	116.7(0.5)	C(5)B–C(6)B–C(7)B	117.3(0.5)
C(4)B–C(5)B–C(6)B	124.9(0.5)	C(1)B–C(8)B–C(9)B	176.8(0.6)
C(2)B–C(7)B–C(6)B	120.6(0.5)	C(8)B–C(9)B–C(14)B	118.9(0.5)
C(8)B–C(9)B–C(10)B	121.9(0.5)	C(9)B–C(10)B–C(11)B	120.9(0.5)
C(10)B–C(9)B–C(14)B	119.2(0.5)	C(10)B–C(11)–C(12)B	120.1(0.5)
O(24)B–C(12)B–C(13)B	123.7(0.5)	O(24)B–C(12)B–C(11)B	115.6(0.5)
C(12)B–C(13)B–C(14)B	118.5(0.5)	C(11)B–C(12)B–C(13)B	120.7(0.5)
O(17)B–C(16)B–O(20)B	124.4(0.5)	C(9)B–C(14)B–C(13)B	120.5(0.5)
O(20)B–C(16)B–N(15)B	126.4(0.5)	O(17)B–C(16)B–N(15)B	109.3(0.5)
O(24)B–C(25)B–C(26)B	107.6(0.5)	O(17)B–C(18)B–C(19)B	111.1(0.6)
C(25)B–C(26)B–C(31)B	119.1(0.7)	C(25)B–C(26)B–C(27)B	120.7(0.6)
C(26)B–C(27)B–C(28)B	120.3(0.6)	C(27)B–C(26)B–C(31)B	120.2(0.5)
C(29)B–C(30)B–C(31)B	120.6(0.6)	C(27)B–C(28)B–C(29)B	120.6(0.6)
C(16)C–O(17)C–C(18)C	115.5(0.4)	C(26)B–C(31)B–C(30)B	118.2(0.6)
C(3)C–N(15)C–C(16)C	125.9(0.5)	C(12)C–O(24)C–C(25)B	117.3(0.5)
C(16)C–N(15)C–H(N15)C	121.7(3.5)	C(3)C–N(15)C–H(N15)C	111.9(3.1)
O(22)C–N(21)C–C(5)C	116.6(0.5)	O(22)C–N(21)C–O(23)C	124.4(0.5)
C(2)C–C(1)C–C(8)C	176.4(0.6)	O(23)C–N(21)C–C(5)C	119.0(0.5)
C(1)C–C(2)C–C(7)C	121.7(0.5)	C(1)C–C(2)C–C(3)C	118.8(0.5)
N(15)C–C(3)C–C(2)C	117.2(0.5)	C(3)C–C(2)C–C(7)C	119.6(0.5)
C(2)C–C(3)C–C(4)C	120.0(0.5)	N(15)C–C(3)C–C(4)C	122.8(0.5)
N(21)C–C(5)C–C(4)C	115.4(0.5)	C(3)C–C(4)C–C(5)C	117.3(0.5)
C(4)C–C(5)C–C(6)C	124.6(0.5)	N(21)C–C(5)C–C(6)C	120.0(0.5)
C(2)C–C(7)C–C(6)C	120.7(0.5)	C(5)C–C(6)C–C(7)C	117.8(0.5)
C(8)C–C(9)C–C(10)C	122.3(0.5)	C(1)C–C(8)C–C(9)C	177.9(0.6)
C(10)C–C(9)C–C(14)C	119.2(0.6)	C(8)C–C(9)C–C(14)C	118.6(0.5)
C(10)C–C(11)C–C(12)C	120.0(0.6)	C(9)C–C(10)C–C(11)C	121.3(0.6)
O(24)C–C(12)C–C(13)C	124.4(0.5)	O(24)C–C(12)C–C(11)C	115.6(0.5)
C(12)C–C(13)C–C(14)C	119.9(0.6)	C(11)C–C(12)C–C(13)C	120.0(0.6)
O(17)C–C(16)C–C(20)C	124.7(0.5)	C(9)C–C(14)C–C(13)C	119.5(0.6)
O(20)C–C(16)C–N(15)C	127.8(0.5)	O(17)C–C(16)C–N(15)C	107.6(0.5)
O(24)C–C(25)C–C(26)C	107.8(0.5)	O(17)C–C(18)C–C(19)C	105.1(0.5)
C(25)C–C(26)C–C(31)C	117.2(0.6)	C(25)C–C(26)C–C(27)C	121.3(0.6)
C(26)C–C(27)C–C(28)C	119.5(0.6)	C(27)C–C(26)C–C(31)C	121.5(0.6)
C(28)C–C(29)C–C(30)C	118.6(0.6)	C(27)C–C(28)C–C(29)C	121.4(0.7)
C(26)C–C(31)C–C(30)C	116.7(0.6)	C(29)C–C(30)C–C(31)C	122.2(0.6)

[a] E.s.d.s shown in parentheses.

crystals. The largest parallel surfaces were found to be $(1\,0\,-1)$ by X-ray diffraction. Since the crystal is monoclinic, the *b* axis and the Y-axis coincide and are found to align in the direction of the pillar. Although the optical Y-axis was in the surface of the measured crystal, X- and Z-axes were not in the surface. The angle between the X-axis and the surface normal was 12° and that of the X-axis and the optic axis was 39° at 532 nm. Assuming that the directions do not depend on the wavelength, n_x and n_z at three wavelengths were calculated from the measured refractive indices in the direction of surface normal. Fig. 3 shows these values and fitted curves of the Sellmeier equation.

Fig. 4(*a*)–(*c*) shows a molecule from the α-form crystal and

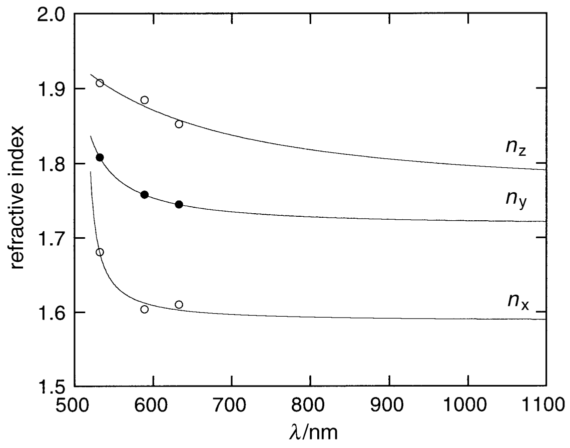

Fig. 3 Refractive indices of **1** in the α-form crystal. Closed circles are the measured value and the open circles are the calculated values. The solid curves denote the value fitted Sellmeier equations.

the packing of the molecules in the crystal lattice viewed along the *b* and *c* axes, respectively. The angle between the two benzene rings bridged by the acetylene moiety is 10.6°. As is clearly seen in Fig. 4(*c*), the molecules in a unit cell are aligned in two directions in the *ab* plane. The angle between them is 88.0° and the angle between a molecule and the *a*-axis is 44.0°. The distance between O(20) and N(15) of the neighbouring molecule one unit cell along the *b*-axis is 2.933(7) Å. The hydrogen bond N(15)–H(N15)···O(20) is formed between two neighbouring molecules, and is therefore expected to be one of the factors that destroys the centrosymmetric structure.

In the β-form crystal, there are three crystallographically independent molecules, which are represented here by molecules A, B, and C. The structures of these molecules are shown in Fig. 5(*a*). For all three molecules, the two benzene rings linked by the triple-bonded carbons are in approximately the same plane, which is almost normal to the *ac* plane. However, the benzene ring in the alkoxy group is tilted 20° from the plane of other benzene rings in molecule A, 74° in the molecule B and 62° in the molecule C. In Fig. 5(*b*), which is the packing diagram of one unit cell viewed along

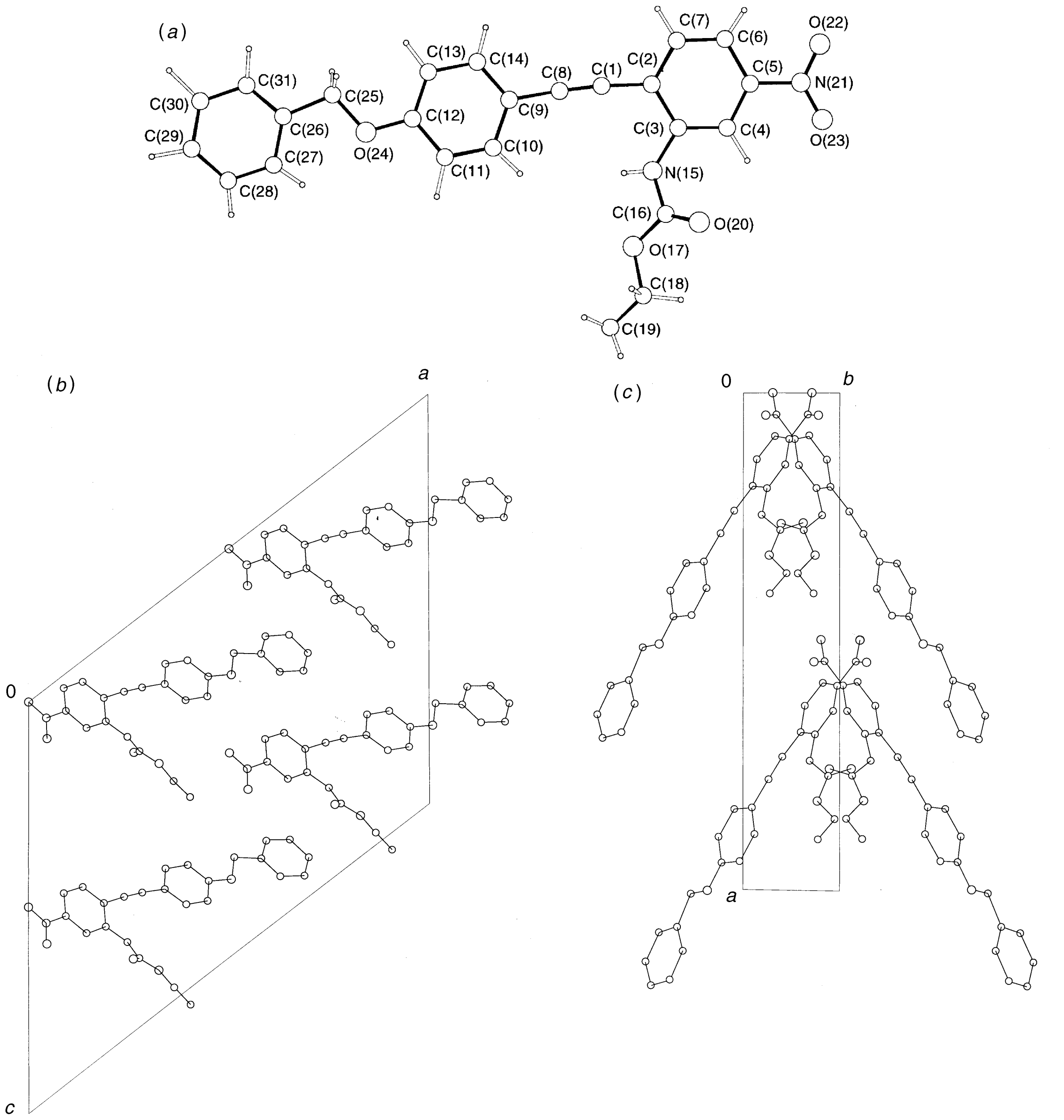

Fig. 4 (*a*) Molecular diagram of the α-form crystal. (*b*) The molecular packing diagram of the α-form crystal viewed along the *b*-axis. (*c*) The molecular packing diagram of the α-form crystal viewed along the *c*-axis.

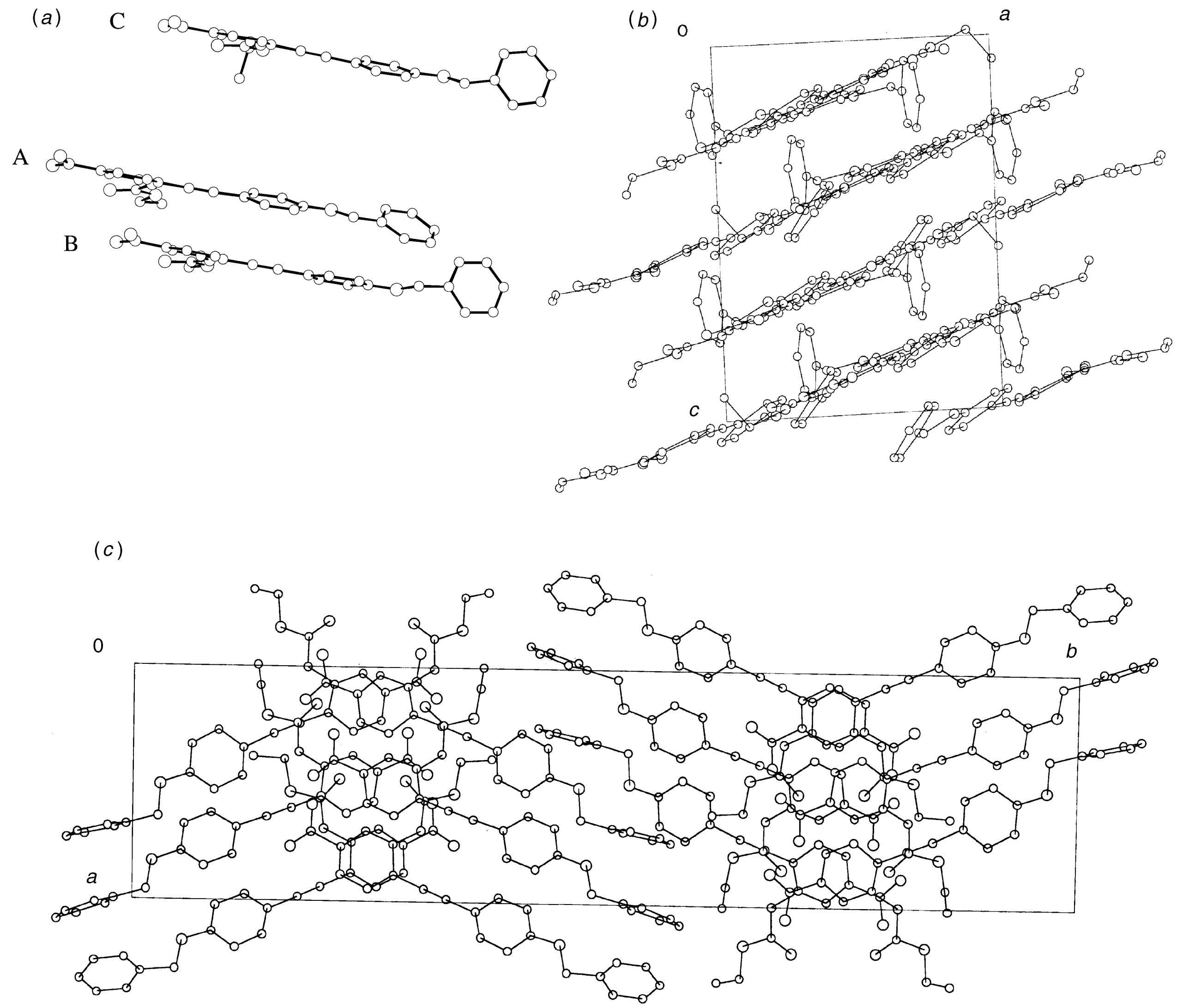

Fig. 5 (*a*) Molecular diagram of the *β*-form crystal. (*b*) The molecular packing diagram of the *β*-form crystal viewed along the *b*-axis. (*c*) The molecular packing diagram of the *β*-form crystal viewed along the *c*-axis.

the *b*-axis, the stacking of the molecules is clear. The view along the *c*-axis is also shown [Fig. 5(*c*)]. The hydrogen atom on N(15) and the neighbouring O(20) are too far apart to form hydrogen bonds. We therefore concluded that the hydrogen bond, which plays an important role in determining the crystal structure, does not exist in the *β*-form crystal.

Molecule **1** is designed to have a large charge transfer between the benzyloxy group and the nitro group through the benzene rings and the triple bond. This charge transfer leads to a large hyperpolarizability. On the other hand, such molecules tend to align antiparallel to each other because of the large ground-state dipole moments. If the molecules were too close to each other they would repulse each other and align in opposite directions. The carbamate group was introduced for steric reasons, so that the molecules do not align and the dipole–dipole interaction is decreased. Additionally, the hydrogen bond between the nitrogen in the amide group and the oxygen in the same group of the next molecule causes the non-centrosymmetric structure, as shown in the *α*-form crystal structure. The carbamate group affects not only the nonlinearity of a molecule but also the crystal structure, as this group makes the molecule bulky and the nonlinear efficiency in the unit volume is decreased. Comparing the recrystallization of the *α*- and *β*-forms from solution, the relative permittivities of the solvents used are different. 2-Ethoxyethanol, from which *α*-form crystallizes, has a larger relative permittivity ($\varepsilon = 29.6$) than ethyl acetate ($\varepsilon = 6.02$). For crystallization of **1**, the strong polar solvent affects the formation of a non-centrosymmetric crystal.[13] Considering that the crystal from a melt is always in the *γ*-form and finally turns into the *β*-form, the *β*-form crystal must be more stable than the others. However, by using a strong polar solvent during the crystal growth it was possible to make a less stable crystal.

The nonlinear optical properties of crystals of **1** were measured using the SHEW technique. The SHEW power from the *β*-form crystal was negligibly small, while on the other hand, the *α*-form crystal showed high SH activity. The SHEW power from the *α*-form crystal was about ten times that from *m*-NA, which means that the nonlinear optical coefficient of **1** should be more than three times that of *m*-NA. Thus compound **1** is expected to be a high SH active material.

Conclusion

We have synthesized ethyl 2-(4-benzyloxyphenylethynyl)-5-nitrobenzene-1-carbamate and studied its polymorphism and crystal structures. Three types of crystal were found which were interchangeable by heating and cooling the sample. One of the crystals, crystallized from a polar solvent, shows non-centrosymmetry, which is induced by the hydrogen bonds between molecules. It is expected to have a large nonlinear optical coefficient which is more than three times that of *meta*-nitroaniline.

We gratefully thank Dr Takashi Kondo and Professor Ryoichi Ito of Tokyo University for their help with refractive index measurements. We thank Dr Takao Tomono of Fuji Xerox Co., Ltd., for his useful comments and advice.

References

1 *Non-linear optical properties of organic and polymeric materials*, ed. D. J. Williams, Am. Chem. Soc. Symp. Ser. 233, American Chemical Society, Washington DC, 1983.

2 *Nonlinear optical properties of organic molecules and crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987.

3 B. F. Levine and C. G. Betha, *J. Chem. Phys.*, 1977, **66**, 1070.

4 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

5 S. J. Lalama and A. F. Garito, *Phys. Rev. A*, 1979, **20**, 1179.

6 (*a*) M. Nakano, K. Yamaguchi and T. Fueno, *Springer Proceedings in Physics*, vol. 36, *Nonlinear Optics of Organics and Semiconductors*, 1989, 98; (*b*) N. Matsuzawa and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 6232; (*c*) T. Kurihara, H. Tabei and T. Kaino, *J. Chem. Soc., Chem. Commun.*, 1987, 959; (*d*) A. E. Stiegman, E. Graham, K. J. Perry, L. R. Khundkar, L.-T. Cheng and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658.

7 (*a*) T. M. Robertson and I. Woodward, *Proc. R. Soc. London, Ser. A*, 1937, **162**, 436; (*b*) S. D. Samarskaya, R. M. Myasnikova and A. I. Kitiagorodkii, *Kristallografiya*, 1968, **13**, 616; (*c*) A. A. Espiritu and J. G. White, *Z. Kristallogr.*, 1977, **147**, 177; (*d*) A. A. Espiritu and J. G. White, *Acta Crystallogr.*, 1977, **B33**, 3899; (*e*) E. M. Graham, V. M. Miskowaski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Shaefer and R. E. Marsho, *J. Am. Chem. Soc.*, 1989, **111**, 8771.

8 M. Kiguchi, M. Kato, N. Kumegawa and Y. Taniguchi, *J. Appl. Phys.*, 1994, **75**, 4332.

9 M. Kiguchi, M. Kato, N. Kumegawa, M. Okunaka and Y. Taniguchi, *Nonlinear Optics*, 1995, **9**, 223.

10 G. W. Gray and B. Jones, *J. Chem. Soc.*, 1954, 1467.

11 A. D. Allen and C. D. Cook, *Can. J. Chem.*, 1963, **41**, 1084.

12 J. J. Blanksma, *Recl. Trav. Chim. Pays-Bas*, 1946, **65**, 329.

13 H. Tabei, T. Kurihara and T. Kaino, *Appl. Phys. Lett.*, 1987, **50**, 1855.

Paper 6/07858C; *Received* 19*th November*, 1996