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The Crystal Structure of Piperidinium *p*-Hydroxybenzoate

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The crystal and molecular structure of piperidinium *p*-hydroxybenzoate, $[C_5H_{10}NH_2]^+[p\text{-}HOC_6H_4CO_2]^-$, has been determined from visually estimated Cu *Kα* data. The crystals are monoclinic, space group *Cc*, $Z=4$, with $a=6·06$, $b=18·35$, $c=10·20$ Å and $\beta=93·0°$. The structure was solved by the convolution molecule and Fourier methods, and refined by the block-diagonal least-squares method to a final *R* value of 0·069 for 1031 non-zero reflexions. Acid and base moieties are held together by two kinds of hydrogen bond (2·69 and 2·80 Å) between piperidinium nitrogen and carboxylate oxygen atoms. An additional hydrogen bond (2·63 Å) from the hydroxyl group at the *para* position to one of the oxygen atoms of the carboxylate ion connects the acid moieties related by a diagonal glide plane. The carboxyl group is twisted from the benzene ring plane by an angle of 16·6°. The piperidine ring takes the chair form.

Introduction

Recently, the crystal structures of the three isomorphous 1:1 addition compounds of *p*-bromo-, *p*-chloro- and *p*-methylbenzoic acids with piperidine have been determined (Kashino, Sumida & Haisa, 1972; Kashino, 1973). The crystal structure analysis of the title compound has been undertaken in order to study the effect of the *p*-hydroxyl group on the hydrogen-bond system in the crystal.

Experimental

The crystals of piperidinium *p*-hydroxybenzoate were prepared by dissolving equimolar quantities of *p*-hydroxybenzoic acid monohydrate and piperidine in ethanol.

Found: C 64·50, H 7·82, N 6·42%. Calculated for $C_{12}H_{17}NO_3$: C 64·52, H 7·68, N 6·27%.

The crystals were transparent plates having well developed {010}. Cell constants were obtained from oscillation and Weissenberg photographs taken with Cu *Kα* radiation ($\lambda=1·5418$ Å). From systematic absences *hkl* when $h+k$ odd, *h*0*l* when *l* odd, the possible space group is *Cc* or *C*2/*c*. However, elementary analysis and density measurements showed that there were four molecular units of the acid and base components in a unit cell, so that the space group was restricted to *Cc* because neither the acid nor the base moiety had $\bar{1}$ or 2 symmetry.

Crystal data: Piperidinium *p*-hydroxybenzoate, $[C_5H_{10}NH_2]^+[p\text{-}HOC_6H_4CO_2]^-$, m.p. 134°C, F.W.

Table 1. *Final atomic parameters and e.s.d.'s* (× 10^4)

The anisotropic temperature factor is defined as $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	−1652 (8)	1814 (2)	1627 (5)	159 (11)	14 (1)	60 (4)	12 (6)	21 (12)	10 (4)
C(2)	−2082 (9)	2240 (2)	2723 (5)	197 (13)	17 (1)	67 (5)	3 (7)	67 (14)	4 (4)
C(3)	−634 (9)	2790 (3)	3139 (5)	217 (15)	19 (1)	71 (5)	7 (7)	47 (15)	−11 (4)
C(4)	1279 (8)	2918 (2)	2481 (5)	186 (13)	15 (1)	60 (4)	−4 (6)	14 (13)	0 (4)
C(5)	1696 (8)	2509 (3)	1376 (5)	179 (14)	20 (1)	71 (5)	−12 (7)	65 (14)	−4 (4)
C(6)	236 (8)	1964 (2)	961 (5)	195 (14)	17 (1)	70 (5)	−12 (7)	71 (15)	−11 (4)
C(7)	−3116 (8)	1181 (2)	1221 (5)	175 (13)	15 (1)	67 (4)	−7 (6)	18 (13)	13 (4)
O(8)	−4440 (6)	940 (2)	2014 (4)	231 (10)	24 (1)	92 (4)	−40 (6)	80 (11)	16 (4)
O(9)	−2875 (7)	913 (2)	95 (4)	263 (11)	18 (1)	73 (3)	−48 (5)	22 (10)	4 (3)
O(10)	2771 (7)	3443 (2)	2848 (4)	261 (11)	23 (1)	84 (4)	−48 (6)	59 (11)	−21 (3)
N(11)	4454 (7)	181 (2)	4264 (4)	178 (11)	17 (1)	75 (4)	15 (6)	52 (12)	8 (3)
C(12)	2417 (10)	−250 (3)	3914 (6)	228 (15)	17 (1)	91 (5)	−2 (7)	33 (15)	3 (4)
C(13)	526 (9)	246 (3)	3490 (6)	197 (14)	27 (2)	105 (7)	−10 (8)	14 (16)	12 (5)
C(14)	97 (9)	781 (3)	4592 (6)	164 (14)	27 (2)	118 (7)	26 (8)	67 (17)	20 (6)
C(15)	2167 (10)	1221 (3)	4948 (7)	240 (16)	20 (1)	130 (7)	32 (8)	48 (19)	−13 (6)
C(16)	4089 (9)	719 (3)	5338 (6)	208 (15)	26 (2)	89 (6)	22 (8)	−1 (16)	−23 (5)

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223.3. Monoclinic, $a=6.06$ (1), $b=18.35$ (1), $c=10{\cdot}20$ (1) Å, $\beta=93{\cdot}0$ (1)°. $D_m=1{\cdot}308$ g cm^{-3} (by flotation), $D_c=1{\cdot}309$ g cm^{-3} (for $Z=4$). Space group *Cc*, $\mu=7{\cdot}8$ cm^{-1} for Cu $K\alpha$ radiation, $F(000)=480$.

Intensities were collected with Cu $K\alpha$ radiation by employing multiple-film equi-inclination Weissenberg techniques for the layers from $0kl$ to $4kl$ and $hk0$ to $hk4$. In all, 1031 reflexions were observed out of about 1280 possible reflexions within the Cu $K\alpha$ sphere. The intensities were estimated visually and corrected for Lorentz and polarization factors and for the spot shape. An extinction correction, $g=3{\cdot}0\times10^{-5}$, was made for the eight strongest reflexions according to the formula $I_{corr}=I_{obs}/(1-gI_{obs})$, but no corrections were made for absorption.

Structure determination and refinement

The orientational and translational parameters of the acid moiety were determined by the convolution molecule method (Ahmed, 1970) which was programmed by Tanaka for the NEAC 2200 N700 computer. The phase angles calculated from the positional parameters of the acid moiety were utilized to evaluate the three-dimensional electron-density distribution, which revealed the piperidine ring. The nitrogen atom was identified by short N· · ·O intermolecular distances. The structure was refined by block-diagonal least-squares calculations (Okaya & Ashida, 1967) with isotropic temperature factors. The positional parameters of 17 hydrogen atoms were calculated by assuming an appropriate geometry, and were included with their appropriate temperature factors, $B=2{\cdot}7$ Å^2, as fixed parameters in subsequent refinement. Further least-squares refinement with anisotropic temperature factors for non-hydrogen atoms reduced the R value to 0·069 for 1031 observed reflexions. The shifts in the positional and thermal parameters were less than $0{\cdot}2\sigma$ and $0{\cdot}8\sigma$ respectively, and the refinement was terminated. The weighting scheme adopted was:

$$w=0{\cdot}5 \qquad \text{for } F_o<F_{\min}(=3{\cdot}7),$$

$$w=1{\cdot}0 \qquad \text{for } F_{\min}\leqq F_o\leqq F_{\max}(=16{\cdot}0)$$

and

$$w=(F_{\max}/F_o)^2 \text{ for } F_{\max}<F_o.$$

At the final stage of the refinement, the difference synthesis was featureless within the range $\pm0{\cdot}4$ eÅ^{-3}. The final atomic parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were performed on a NEAC 2200–N700 computer at the Computation Center of Osaka University and on a NEAC 2200–500 computer at Okayama University Computer Center.

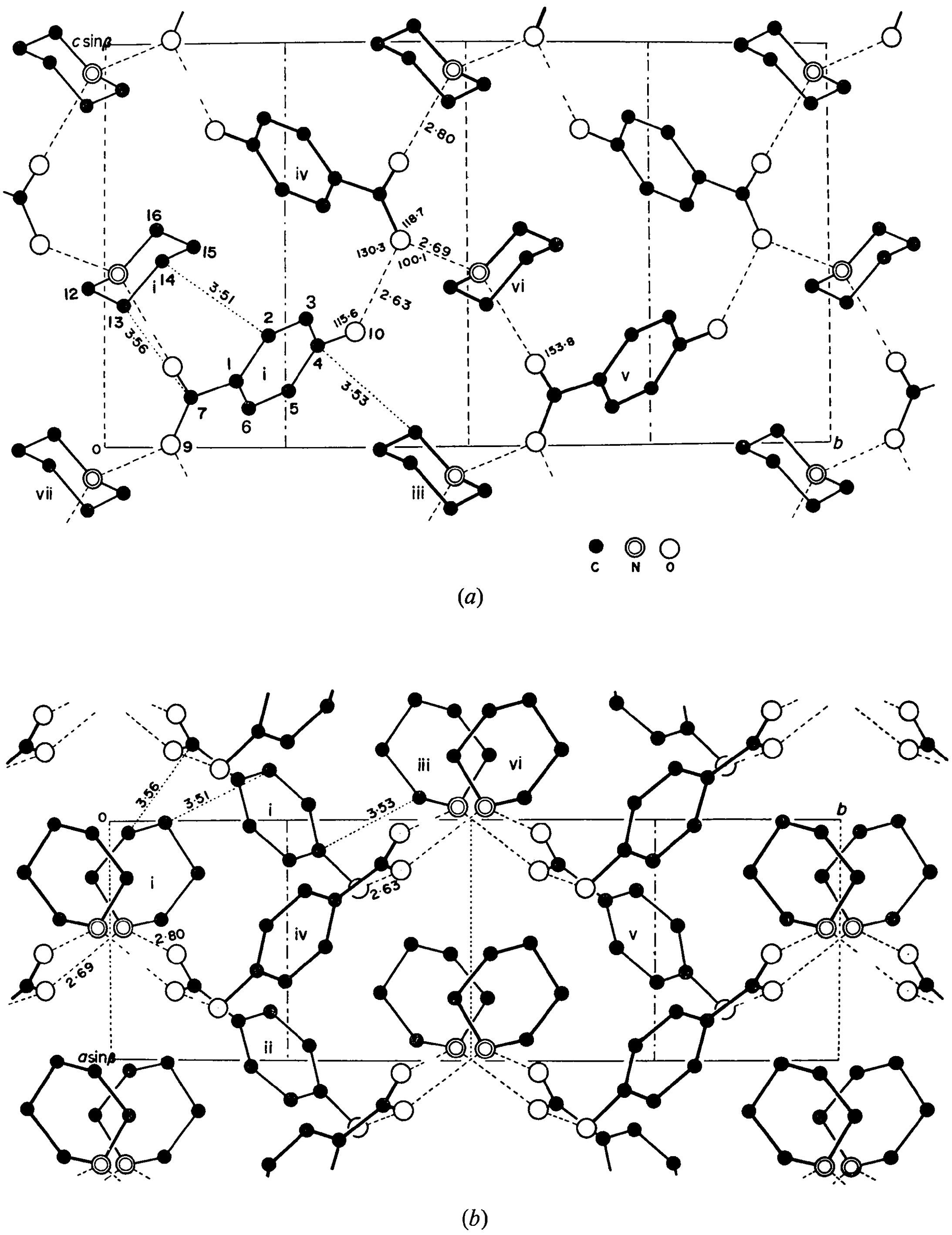
Table 2. *Observed and calculated structure factors* (× 5)

Unobserved reflexions are marked with an asterisk.

[illegible]

Description of the structure and discussion

The projections of the structure are presented in Fig. 1. Some short intermolecular distances and coordination angles around the oxygen atoms are indicated in the figures. Coordination angles around the nitrogen atom are listed in Table 3 and intermolecular distances in Table 4. Acid and base moieties are held together by two kinds of hydrogen bond (2·69 and 2·80 Å) between piperidinium nitrogen and carboxylate oxygen atoms. An additional hydrogen bond (2·63 Å) from the hydroxyl group in the *para* position to one of the oxygen atoms of the carboxylate ion connects the acid moieties related by a diagonal glide plane, thus forming a three-dimensional hydrogen-bond network. The structure satisfies the principle of maximum hydrogen bonding and consists of a close-packed array of the moieties. The nitrogen atom is approximately tetrahedrally surrounded by the atoms C(12), C(16), O(8) and O(9), as found previously in related compounds (Kashino, Sumida & Haisa, 1972; Kashino, Sasaki & Haisa, 1973; Kashino, 1973). However, in the present case, the N· · ·O(8) bond length, 2·80 Å, with nearly tetrahedral C–N· · ·O angles, 108·8 and 107·4°, is rather longer than the N· · ·O(9) bond length, 2·69 Å, with C–N· · ·O angles of 99·0 and 111·8°. This lengthening may be caused by the intermolecular contacts C(2$^{\text{i}}$)· · ·C(14$^{\text{i}}$) and C(7$^{\text{i}}$)· · ·C(13$^{\text{i}}$). The C(4)–O(10)· · ·O(9) angle is 115·6°, close to the corresponding angle found in *p*-hydroxybenzoic acid monohydrate (Fukuyama, Ohkura, Kashino & Haisa, 1973). The least-squares planes are given in Table 5. The dihedral angle between the benzene ring and the plane of the carboxylate group is 16·6°. The hydrogen-bond formation seems to be favoured by this large twist, as found in piperazinium terephthalate (Kashino, Sasaki & Haisa, 1973). The C(1)–C(7) and C(4)–O(10) bonds bend to the same side out of the benzene ring plane as in the *p*-



(a)

(b)

Fig. 1. The crystal structure of piperidinium *p*-hydroxybenzoate: (*a*) viewed along [100], (*b*) viewed along [001]. Broken lines show hydrogen bonds, and dotted lines intermolecular contacts. Key to molecules:

i	x	y	z	ii	$1+x$	y	z	iii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
iv	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	v	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z	vi	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	z
vii	$-1+x$	$-y$	$-\frac{1}{2}+z$.								

hydroxybenzoic acid monohydrate. In the piperidinium ion, atoms C(12), C(13), C(15) and C(16) form a plane within 0·009 Å, whereas in (±)-α-promedol alcohol (Ahmed & De Camp, 1972) and (±)-β-promedol alcohol (De Camp & Ahmed, 1972), which have a piperidine ring with large substituents, the corresponding values amount to 0·03–0·05 Å. The atom N(11) deviates from the plane by 0·661 Å, the atom C(14) by −0·689 Å, and the piperidine ring takes the chair form.

The bond lengths and angles are listed in Table 6. No significant differences are observed between the C(7)–O(8) and C(7)–O(9) bond lengths, in accordance

Table 3. *Coordination angles* (°) *around the nitrogen atom*

Atomic numbering and the symmetry code are given in Fig. 1.

O(8^{v}) –N(11^{vi})–C(12^{vi})	107·4 (3)
O(8^{v}) –N(11^{vi})–C(16^{vi})	108·8 (3)
O(9^{iv})–N(11^{vi})–C(12^{vi})	99·0 (3)
O(9^{iv})–N(11^{vi})–C(16^{vi})	111·8 (3)
O(8^{v}) –N(11^{vi})–O(9^{iv})	117·7 (2)

Table 4. *Intermolecular distances* (Å)

Atomic numbering and the symmetry code are given in Fig. 1.

(*a*) Hydrogen bonds

N(11^{i})···O(8^{ii})	2·796 (6)
O(9^{i})···N(11^{vii})	2·688 (6)
O(9^{i})···O(10^{iii})	2·626 (6)

(*b*) Other intermolecular distances

C(1^{i})···C(13^{i})	3·657 (8)
C(1^{i})···C(14^{i})	3·678 (8)
C(7^{i})···C(13^{i})	3·555 (8)
C(2^{i})···C(14^{i})	3·505 (8)
C(4^{i})···C(16^{iii})	3·534 (8)
O(9^{i})···C(12^{vii})	3·273 (7)
C(7^{i})···N(11^{vii})	3·478 (7)

Table 6. *Bond lengths* (Å) *and angles* (°)

The e.s.d.'s are given in parentheses.

C(1)—C(2)	1·399 (7)
C(2)—C(3)	1·388 (7)
C(3)—C(4)	1·390 (7)
C(4)—C(5)	1·387 (7)
C(5)—C(6)	1·388 (7)
C(6)—C(1)	1·389 (7)
C(1)—C(7)	1·506 (7)
C(7)—O(8)	1·250 (6)
C(7)—O(9)	1·266 (6)
C(4)—O(10)	1·360 (6)
N(11)–C(12)	1·494 (7)
N(11)–C(16)	1·501 (7)
C(12)–C(13)	1·509 (8)
C(13)–C(14)	1·525 (9)
C(14)–C(15)	1·519 (9)
C(15)–C(16)	1·521 (9)
C(1)—C(2)—C(3)	120·6 (5)
C(2)—C(3)—C(4)	120·3 (5)
C(3)—C(4)—C(5)	119·5 (5)
C(4)—C(5)—C(6)	119·8 (5)
C(5)—C(6)—C(1)	121·4 (5)
C(6)—C(1)—C(2)	118·2 (5)
C(3)—C(4)—O(10)	123·1 (5)
C(5)—C(4)—O(10)	117·4 (5)
C(2)—C(1)—C(7)	121·3 (4)
C(6)—C(1)—C(7)	120·4 (4)
C(1)—C(7)—O(8)	118·9 (4)
C(1)—C(7)—O(9)	117·0 (4)
O(8)—C(7)—O(9)	124·0 (5)
N(11)–C(12)–C(13)	110·7 (5)
C(12)–C(13)–C(14)	109·5 (5)
C(13)–C(14)–C(15)	110·3 (5)
C(14)–C(15)–C(16)	110·6 (5)
C(15)–C(16)–N(11)	110·3 (5)
C(16)–N(11)–C(12)	111·8 (4)

Table 5. *Least-squares planes*

Each plane is represented by $lX+mY+nZ=p$, where $X=ax+cz\cos\beta$, $Y=by$ and $Z=cz\sin\beta$, in Å.

(1) Best plane through the benzene ring		(2) Best plane through C(1), C(7), O(8), O(9)		(3) Best plane through C(12), C(13), C(15), C(16)	
l	0·4759	*l*	0·6776	*l*	0·5524
m	−0·6568	*m*	−0·6296	*m*	0·3395
n	0·5849	*n*	0·3801	*n*	−0·7613
p	−1·7448	*p*	−2·2061	*p*	−2·4887
	Deviation (Å)		Deviation (Å)		Deviation (Å)
C(1)	0·010	C(1)	0·003	C(12)	−0·009
C(2)	−0·002	C(7)	−0·010	C(13)	0·009
C(3)	−0·009	O(8)	0·004	C(15)	−0·009
C(4)	0·013	O(9)	0·004	C(16)	0·009
C(5)	−0·005				
C(6)	−0·006				
	Distance from the above plane (Å)				Distance from the above plane (Å)
C(7)	0·119			N(11)	0·661
O(8)	0·480			C(14)	−0·689
O(9)	−0·131				
O(10)	0·020				

with the fact that the carboxyl group is ionized. No C–C bond lengths in the benzene ring deviate significantly from the mean value of 1.390 Å. The bond length of C(4)–O(10), 1·360 Å, accords with the corresponding one in *p*-hydroxybenzoic acid monohydrate. The angle O(10)–C(4)–C(5), 117·4°, is smaller than that of O(10)–C(4)–C(3), 123·3°, as observed in the monohydrate. The mean values of the C–C and C–N bond lengths in the piperidine ring are 1·519 and 1·498 Å, respectively. These values are in accordance with 1·505 and 1·497 Å in piperidine hydrochloride (Rérat, 1960), and 1·522 and 1·499 Å in 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (Berliner, 1970), respectively. The bond angles in the piperidine ring are slightly larger than the regular tetrahedral angle.

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The Crystal Structure of Sr_5Sb_3

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Sr_5Sb_3 crystallizes as a Mn_5Si_3-type structure, space group $P6_3/mcm$, with two formula units in a cell of dimensions $a=9{\cdot}496\pm0{\cdot}005$, $c=7{\cdot}422\pm0{\cdot}005$ Å. The calculated density is 4·602 g cm^{-3}. The structure of Sr_5Sb_3 has been determined by three-dimensional Patterson synthesis. The positional and isotropic thermal parameters were refined by least-squares analysis, yielding a final R value of 0·056. There is one unusually short distance Sr–Sr in chains parallel to the c axis.

Introduction

The binary system Sr–Sb was treated by Shchukarev, Morozova & Kan Kho-in (1957*a*, *b*) in a preliminary study. Metallographic observations of cast alloys, thermal analysis and gram-formula volume *vs.* composition curves indicated the existence of four intermediate phases corresponding to the compounds $SrSb_3$, SrSb, Sr_3Sb_2 and Sr_2Sb. More recently, Brauer & Müller (1961) have reported on a compound with tetragonal symmetry and formula Sr_2Sb.

We prepared new samples of Sr-rich alloys in order to solve the crystal structure of the last compound. Powder X-ray diffraction patterns of those samples demonstrated the existence of two compounds in the alloys. One of them, in agreement with Brauer & Müller (1961), belongs to the tetragonal system. The other compound of the mixture is not tetragonal; the present paper reports on its crystal structure. From this study the formula Sr_5Sb_3 was deduced for this compound.

Experimental

Single crystals of Sr_5Sb_3 were prepared by cooling a melt of stoichiometry 4Sr + 1Sb from 1430°C to room temperature in argon atmosphere with subsequent leaching of the alloy with anhydrous ammonia. Under these conditions the excess of Sr is removed and separated black crystals of Sr_5Sb_3 with nearly prismatic shape were obtained. They are hard and extremely sensitive to air. Thus they had to be kept under argon. The elements used for synthesis had stated purities of 99% (Sr) and 99·99% (Sb).

The symmetry, space group and approximate lattice parameters were determined from Weissenberg photographs taken with Cu $K\alpha$ radiation. Sr_5Sb_3 was found to be hexagonal with two formula units in the cell. The systematic absences correspond to three space groups, $P6_3cm$, $P\bar{6}c2$ and $P6_3/mcm$. No piezoelectric properties were found, and the results of the E-value distribution did not conclusively differentiate between centrosymmetric and non-centrosymmetric structures. Anal-