calculations for aniline (Niu & Boggs, 1984) found that the C—N bond lies in the aromatic plane when the dihedral angle between the N lone-pair orbital and the aromatic π orbitals is 90° and that the out-of-plane angle for the C—N bond increases to 2·4° when the dihedral angle between the orbitals is 0°. The maximum out-of-plane angle for the C(aryl)—N bonds in the *o*- and *p*-chlorophenyl compounds is at N(3) in the *p*-chlorophenyl compound, where the N lone-pair/π-orbital dihedral angle is 0°, in qualitative agreement with the MO calculations.

The CH_2—N—CH_2 angles in the triazacyclohexane rings are 109·3–110·8 (2)° (*o*-Cl compound) and 108·7–110·6 (5)° (*p*-Cl compound), and the N—CH_2—N angles are 112·0–113·4 (3)° (*o*-Cl compound) and 110·5—112·0 (6)° (*p*-Cl compound). There are similar small differences in the *o*-, *m*- and *p*-fluorophenyl compounds where the CH_2—N—CH_2 angles are 108·2–110·7° and the N—CH_2—N angles are 110·5–113·0°. The torsion angles around the C—N bonds in the triazacyclohexane rings are 55·0–56·7 (2)° (*o*-Cl compound) and 55·6–58·9 (5)° (*p*-Cl compound).

In solution, facile conformational interconversion in both compounds results in averaging of the ^{1}H NMR signals of the axial and equatorial CH_2 H atoms, which appear as a narrow singlet at *ca* δ 4·7 ($CDCl_3$).

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Structures of (Methyl)phenylhydrazone Derivatives and their Nonlinear Optical Properties

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Abstract. The crystal structures of two (methyl)-phenylhydrazone derivatives, which showed very different second-harmonic generation (SHG) efficiencies, were determined by X-ray diffraction at room temperature with Mo $K\alpha$ radiation (λ = 0·7107 Å). 3-Methylbenzaldehyde *N*-methyl-*N*-phenylhydrazone (Me-BMPH): $C_{15}H_{16}N_2$, M_r = 224·3, monoclinic, $P2_1/a$, a = 12·106 (3), b = 18·398 (8), c = 5·800 (2) Å, β = 91·92 (2)°, V = 1291·1 (7) Å^3, Z = 4, D_x = 1·154, D_m = 1·160 g cm^{-3} (293 K), μ = 0·64 cm^{-1}, $F(000)$ = 480; the final R was 0·056 for 1421 significant observed reflections. 3-Methoxybenzaldehyde *N*-methyl-*N*-phenylhydrazone (MeO-BMPH): $C_{15}H_{16}N_2O$, M_r = 240·3, monoclinic, $P2_1$, a = 13·975 (2), b = 7·953 (1), c = 5·933 (1) Å, β = 96·81 (1)°, V = 654·8 (2) Å^3, Z = 2, D_x = 1·219, D_m = 1·221 g cm^{-3} (293 K), μ = 0·73 cm^{-1}, $F(000)$ = 256; the final R was 0·053 for 748 significant observed reflections. The SHG efficiency, measured on a powder sample, is nearly zero for Me-BMPH, whereas it is 12·5 times that of urea standard for MeO-BMPH. Both molecules are nearly

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planar and have large hyperpolarizabilities. The formation of a centrosymmetric structure gives rise to no SHG response in Me-BMPH.

Introduction. 3-Methylbenzaldehyde *N*-methyl-*N*-phenylhydrazone (Me-BMPH) and 3-methoxybenzaldehyde *N*-methyl-*N*-phenylhydrazone (MeO-BMPH) are composed of non-centrosymmetric molecules, which resemble each other in structure and electronic states, whereas the SHG (second-harmonic generation) efficiency of MeO-BMPH was found to be 12·5 times that of urea standard, while Me-BMPH showed no effect. It is known that the SHG efficiency is related not only to the hyperpolarizability β of a molecule but to the space symmetry of the crystal. In order to confirm these points, the crystal structures of the two compounds were determined by X-ray diffraction and the β values were calculated with the MO-MNDO method.

Experimental. Single crystals of the compounds were obtained by slow evaporation from acetone solution. Their densities D_m were measured by flotation. A Rigaku AFC-5 diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) was used. Lattice parameters were determined by least squares from 25 reflections with $25 \le 2\theta \le 37°$. The intensity of each reflection was measured up to $2\theta = 55°$. Me-BMPH: crystal size 0·25 × 0·25 × 0·35 mm, ω–2θ scan mode, ω-scan width $(1{\cdot}1 + 0{\cdot}4\tan\theta)°$, scan speed 3° min^{-1}. 3657 reflections were measured, and 1421 of them $[F_o \ge 3\sigma(F_o)]$ were used for structure determination, index range h −15 to 15, k 0 to 23, l 0 to 7. Three standard reflections (602, 4,10,3 and $\bar{4}54$) were monitored every 200 measurements, ±2·7% variation in intensity. MeO-BMPH: crystal size 0·28 × 0·43 × 0·50 mm, ω–2θ scan mode, ω-scan width $(1{\cdot}0 + 0{\cdot}5\tan\theta)°$, scan speed 6° min^{-1}. 1669 reflections were measured, and 748 of them $[F_o \ge 3\sigma(F_o)]$ were used for structure determination, index range h −18 to 18, k 0 to 10, l 0 to 7. Three standard reflections ($\bar{2}42$, $\bar{1}\bar{2}$,0,1 and 450) were monitored every 200 measurements, ±1·8% variation in intensity.

Intensities were corrected for Lp but not for absorption. The structures were solved by direct methods with *MULTAN* (Main, Woolfson & Germain, 1971). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Locations of H atoms were found from difference Fourier maps. The scale factor, positional and anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms were refined by full-matrix least-squares program *FLS*80 in *UNICS*III (Sakurai & Kobayashi, 1979), providing $\sum w(|F_o| - |F_c|)^2$ was minimized where $w = 1/|\sigma(F_o)|^2$. In the process of refinement, the multiplicities for the six H atoms connected to the C(17) atom in Me-BMPH are fixed at 0·5 and others at unity. The final R was 0·056, $wR = 0{\cdot}047$, $S = 1{\cdot}87$, $(\Delta/\sigma)_{max} = 0{\cdot}31$, $(\Delta\rho)_{max} = +0{\cdot}132$ and $(\Delta\rho)_{min} = -0{\cdot}141$ e Å^{-3} for Me-BMPH and the final R was 0·053, $wR = 0{\cdot}061$, $S = 1{\cdot}64$, $(\Delta/\sigma)_{max} = 0{\cdot}10$, $(\Delta\rho)_{max} = +0{\cdot}101$ and $(\Delta\rho)_{min} = -0{\cdot}185$ e Å^{-3} for MeO-BMPH. Definition of origin for MeO-BMPH by fixing the y coordinate of the O(17) atom.

The SHG efficiencies were measured by Kurtz & Perry's powder technique (Kurtz & Perry, 1968). The values of hyperpolarizability β were obtained from Oudar's two-level approximation (Oudar & Chemla, 1977). The coefficients of the molecular orbitals were calculated by use of the program package *AMPAC* [QCPE #523 (original version: Dewar & Stewart, 1986; modified version: Lynn, Pierce & Raynolds, 1987)], using the MNDO approximation (Dewar & Thiel, 1977). In these calculations, each molecular geometry was optimized for an assumed planar molecule. The dipole moments were calculated by *AMPAC* and the oscillator strength by our computing program. The interaction between the two lowest singly occupied excited configurations was involved in the calculation of the excited states. The transition energy was obtained experimentally from the wavelength at the maximal electronic absorption band.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters of Me-BMPH and MeO-BMPH for non-H atoms are shown in Tables 1 and 2, respectively.* The molecules are illustrated by *ORTEP* (Johnson, 1965) in Figs. 1 and 2. The packing arrangements of the molecules are shown in Figs. 3 and 4.

Least-squares-planes calculations showed that the C(17) atom is shifted by −0·024 (5) Å from the benzene plane in Me-BMPH, and the O(17) and C(18) atoms are shifted by −0·028 (6) and 0·010 (8) Å, respectively, in MeO-BMPH. The N(7) atom is shifted by 0·002 (2) and −0·015 (5) Å from the C(1)—C(9)—N(8) plane in Me-BMPH and MeO-BMPH, respectively. The hydrazone skeleton was found to be almost planar for both compounds. Therefore, for the present molecules, the possibility of inducing an intramolecular charge-transfer interaction (Tosi, Cardellini & Bocelli, 1988) is expected. Selected dihedral angles at the corners of several planar parts of the molecules are shown in Table 3. Bond lengths and angles of the present molecules are listed in Table 4. Generally, bond lengths in conju-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52286 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and* B_{eq} ($Å^2 \times 10^2$) *values of Me-BMPH, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	1597 (2)	549 (1)	6161 (4)	468 (7)
C(2)	1706 (3)	127 (2)	8123 (5)	698 (11)
C(3)	2617 (3)	−307 (2)	8531 (6)	769 (12)
C(4)	3437 (3)	−346 (2)	6994 (6)	662 (10)
C(5)	3356 (3)	84 (2)	5059 (6)	605 (10)
C(6)	2452 (2)	526 (2)	4626 (5)	508 (8)
N(7)	661 (2)	979 (1)	5713 (4)	571 (7)
N(8)	721 (2)	1458 (1)	3926 (4)	486 (6)
C(9)	−325 (3)	925 (2)	7074 (7)	675 (12)
C(10)	−67 (2)	1905 (2)	3487 (5)	509 (8)
C(11)	16 (2)	2426 (1)	1602 (4)	474 (7)
C(12)	914 (2)	2436 (2)	157 (5)	498 (8)
C(13)	978 (2)	2928 (2)	−1633 (5)	526 (8)
C(14)	115 (3)	3416 (2)	−1980 (6)	640 (10)
C(15)	−774 (3)	3417 (2)	−568 (6)	701 (11)
C(16)	−823 (3)	2932 (2)	1219 (6)	609 (10)
C(17)	1963 (3)	2932 (3)	−3155 (7)	663 (12)

Table 2. *Atomic coordinates* ($\times 10^4$) *and* B_{eq} ($Å^2 \times 10^2$) *values of MeO-BMPH, with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	9650 (2)	6559 (6)	6860 (6)	411 (10)
C(2)	10406 (3)	7364 (8)	6022 (9)	521 (13)
C(3)	11315 (3)	7269 (7)	7153 (9)	596 (15)
C(4)	11514 (3)	6409 (8)	9126 (8)	568 (14)
C(5)	10765 (3)	5600 (7)	9988 (8)	543 (13)
C(6)	9839 (3)	5672 (7)	8860 (7)	462 (12)
N(7)	8709 (2)	6635 (6)	5711 (5)	501 (10)
N(8)	7999 (2)	5975 (6)	6832 (5)	475 (9)
C(9)	8489 (4)	7302 (10)	3477 (8)	651 (17)
C(10)	7114 (3)	6005 (6)	5928 (8)	449 (11)
C(11)	6365 (2)	5266 (6)	7119 (6)	417 (10)
C(12)	6567 (3)	4439 (7)	9175 (7)	470 (12)
C(13)	5838 (3)	3697 (7)	10184 (8)	533 (13)
C(14)	4893 (3)	3785 (7)	9200 (7)	512 (13)
C(15)	4679 (2)	4633 (7)	7169 (6)	436 (11)
C(16)	5409 (3)	5369 (7)	6131 (7)	438 (12)
O(17)	3726 (2)	4685	6343 (5)	590 (9)
C(18)	3464 (4)	5489 (10)	4219 (9)	669 (17)

gated systems are longer than double bonds and shorter than single bonds. Indeed, for both compounds, N(7)—N(8) and C(10)—C(11) are shorter than a typical single bond and N(8)=C(10) is longer than a typical double bond. It is therefore suggested that an extended π-electron conjugated system is induced in the N(7)—N(8)=C(10)—Ph group.

The molecular orbital calculations gave the large β values as $25{\cdot}276 \times 10^{-30}$ and $22{\cdot}907 \times 10^{-30}$ esu ($8{\cdot}431 \times 10^{-35}$ and $7{\cdot}641 \times 10^{-35}$ C m^{-2}) (at $\lambda = 1{\cdot}064$ μm) for Me-BMPH and MeO-BMPH respectively, owing to the large difference in dipole moment between the excited and the ground states, which was caused by the charge transfer in the extended π-electron conjugated system. The slight difference in the β value cannot explain the remarkable difference in SHG efficiency between the two

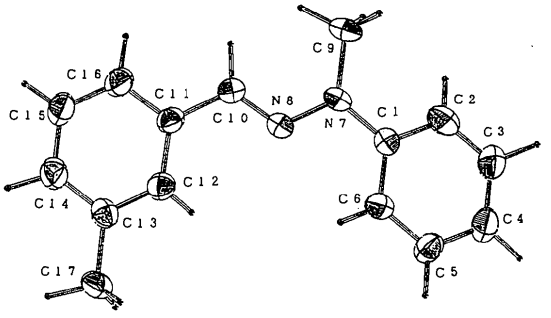

Fig. 1. 3-Methylbenzaldehyde *N*-methyl-*N*-phenylhydrazone (Me-BMPH).

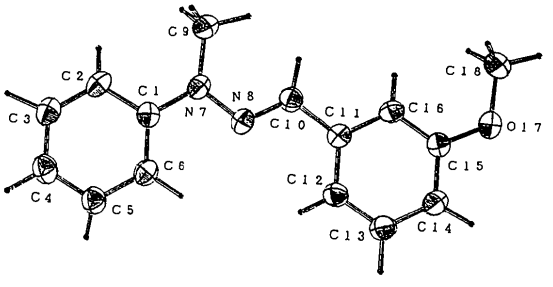

Fig. 2. 3-Methoxybenzaldehyde *N*-methyl-*N*-phenylhydrazone (MeO-BMPH).

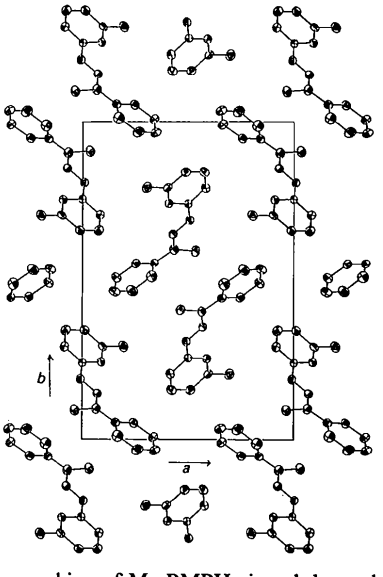

Fig. 3. The packing of Me-BMPH viewed down the *c* axis.

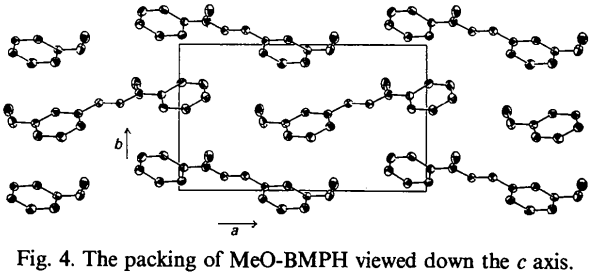

Fig. 4. The packing of MeO-BMPH viewed down the *c* axis.

Table 3. *Selected dihedral angles* (°) *between least-squares planes*

Planes: *A* C1···C6; *B* C11···C16; *C* C1, N7, N8; *D* N7, N8, C10; *E* N8, C10, C11.

	Me-BMPH	MeO-BMPH
A—B	9·2	4·0
A—C	10·6	7·9
B—E	3·0	3·5
C—D	4·5	0·8
D—E	1·3	1·3

Table 4. *Bond lengths* (Å) *and angles* (°) *for Me-BMPH and MeO-BMPH, with e.s.d.'s in parentheses*

	Me-BMPH	MeO-BMPH
C(1)···C(6)*	1·376 (5)	1·374 (8)
C(11)···C(16)*	1·383 (4)	1·383 (8)
C(1)—N(7)	1·400 (3)	1·409 (7)
N(7)—N(8)	1·364 (3)	1·363 (7)
N(8)—C(10)	1·279 (4)	1·289 (7)
C(10)—C(11)	1·459 (4)	1·454 (7)
N(7)—C(9)	1·457 (5)	1·427 (10)
C(13)—C(17)	1·508 (6)	
C(15)—O(17)		1·365 (9)
O(17)—C(18)		1·422 (10)
C(1)···C(6)*	120·0 (3)	120·0 (5)
C(11)···C(16)*	120·0 (3)	120·0 (5)
C(1)—N(7)—N(8)	116·3 (2)	116·0 (4)
C(1)—N(7)—C(9)	122·3 (3)	123·4 (5)
N(8)—N(7)—C(9)	121·4 (3)	120·5 (5)
N(7)—N(8)—C(10)	120·5 (2)	120·5 (5)
N(8)—C(10)—C(11)	120·1 (3)	120·0 (5)

* The average for a benzene ring.

crystals. It is concluded that the prominent decrease of the SHG efficiency in Me-BMPH is due to the packing mode of the molecules.

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Structure of a Cyclopropaneaziridine Derivative of 1,5-Naphthyridine

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Abstract. 1,2-Bis(dimethylaminosulfonyl)-1,1a,1b,2-tetrahydroaziridino[1,2-*a*]cyclopropano[*c*][1,5]naphthyridine, $C_{14}H_{20}N_4O_4S_2$, $M_r = 372{\cdot}5$, triclinic, $P\bar{1}$, $a = 8{\cdot}645$ (2), $b = 10{\cdot}340$ (1), $c = 12{\cdot}441$ (1) Å, $\alpha = 94{\cdot}65$ (1), $\beta = 106{\cdot}53$ (2), $\gamma = 119{\cdot}97$ (2)°, $V = 889{\cdot}6$ Å^3, $Z = 2$, $D_m = 1{\cdot}32$, $D_x = 1{\cdot}390$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 28{\cdot}1$ cm^{-1}, $F(000) = 392$, $T = 293$ K, $R = 0{\cdot}0438$ for 3399 reflections. The structure of the title compound is compared with the previously described 1,8 isomer. The two isomers have different conformations for the sulfonamide groups.

Introduction. Aziridine derivatives have attracted attention because of their antitumor (Dermer & Ham, 1969), antibiotic (Athar, Begleiter, Jonson, Lown, McLaughlin & Sim, 1975), and insect chemosterilant properties (Haynes, Mattix, Mitlin,

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