urea standard. For the successful engineering of organic crystals with a high second-order nonlinear response, both microscopic and macroscopic properties must be considered. On the molecular level, it is the hyperpolarizability $\beta$ in the expansion (Zernike & Midwinter, 1973)

$$\mu = \alpha E + \beta E^2 + \gamma E^3 + \ldots$$

which must be made large. Although centrosymmetry is the rigorous requirement for total cancellation of all molecular $\beta$ components, nonrigorous partial cancellation is generally the rule for noncentrosymmetric point groups. The ability of the components of $\beta$ to be reflected in the SHG efficiency of the crystal depends upon the orientation of the molecules in the unit cell (Williams, 1984).

With the CNDO/2 method (Pople & Segal, 1966), the calculated dipole moment was found to be $30{\cdot}7 \times 10^{-30}$ Cm. The dipole-moment vector makes 72·1, 18·9 and 84·4° with axes *a*, *b* and *c* of the crystal. These values are far from the theoretically calculated favourable angle of 54·7° for nonlinear interactions for crystals belonging to the point group 222 (Oudar & Zyss, 1982). Further, it has been theoretically estimated that point groups 1, 2, *m* and *mm*2 correspond to the highest possible phase-matchable coefficients while other symmetry groups are less favourable. But 3-methyl-4-nitropyridine 1-oxide, which belongs to space group $P2_12_12_1$ (Shiro, Yamakawa & Kubota, 1977), exhibits high SHG efficiency (Zyss, Chemla & Nicoud, 1981). One of the important factors enhancing SHG activity is a high $\Delta\mu$, the difference between the excited charge-transfer and ground-state dipole moments. The hyperpolarizability $\beta$ of a molecule is directly proportional to $\Delta\mu$ (Zyss & Berthier, 1982).

We have no information on the excited-state dipole moment of the title molecule. However, it is surmised that $\Delta\mu$ is unlikely to be significant, the SHG efficiency being very low.

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# 7-Benzyloxy-9-methylenebicyclo[3.3.1]non-3-en-2-one

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**Abstract.** $C_{17}H_{18}O_2$, $M_r = 254{\cdot}31$, orthorhombic, $Pbn2_1$, $a = 11{\cdot}276\,(2)$, $b = 12{\cdot}414\,(3)$, $c = 9{\cdot}864\,(2)$ Å, $V = 1380{\cdot}8\,(4)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}21\,(1)$, $D_x = 1{\cdot}22$ g cm$^{-3}$, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}867$ cm$^{-1}$, $F(000) = 544$, room temperature, $R = 0{\cdot}045$ for 1510 observed reflections. The six-membered ring having the benzyloxy group in the axial position takes a slightly flattened chair conformation. The other

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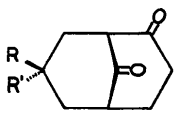
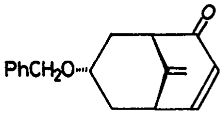
six-membered ring has an α,β-unsaturated carbonyl group and is in a half-chair conformation.

**Introduction.** The reaction of a cyclohexanone morpholine enamine with an acryl chloride is one of the useful methods for constructing a bicyclo[3.3.1]nonane framework (Hickmott & Hargreaves, 1967). From a similar reaction of 4-benzyloxy-1-morpholinocyclohexene according to the procedure reported by Aredova, Sevost'Yanova, Krayushkin, Novikov & Karpenko (1976), we found that two isomers (1*a*) and (1*b*) [(1*a*)/(1*b*) = 3:1] were obtained in 80% yield. The orientation of the 7-benzyloxy group in the major isomer (1*a*) was estimated to be axial from $^1$H NMR spectra.* When (1*a*) was treated successively with trimethylsilyl triflate [$CF_3SO_3Si(CH_3)_3$], $Ph_3P{=}CH_2$, and $Pd(OAc)_2$, a crystalline α,β-unsaturated carbonyl compound (2) [C(7)—H absorbs at 3·77 p.p.m. as a broad singlet] was obtained. In order to confirm the configuration of the benzyloxy group, the crystal structure of the title compound (2) is reported here.



(1*a*) R=H, R'=OCH₂Ph

(1*b*) R=OCH₂Ph, R'=H



(2)

**Experimental.** Colorless columns recrystallized from hexane, $D_m$ by flotation in aqueous KI solution; systematic absences (from Weissenberg photographs) $h0l$ for $h+l = 2n$ and $0kl$ for $k = 2n$ and $Z = 4$, space group $Pbn2_1$; crystal 0·75 × 0·43 × 0·45 mm; Rigaku AFC-5 automated four-circle diffractometer, 40 kV and 160 mA; unit-cell dimensions by least-squares refinement from 25 reflections with $19 < 2\theta < 21°$; $2\theta$–$\omega$ scans, scan rate 2° min$^{-1}$, $\Delta\omega = (1{\cdot}5 + 0{\cdot}5\tan\theta)°$; three standard reflections measured every 56 reflections with ±1% fluctuation; 1991 unique reflections, $2\theta = 70°$ ($0 \le h \le 18$, $0 \le k \le 20$, $0 \le l \le 15$); 1512 reflections with $|F_o| > 3\sigma(F_o)$ used for structure determination; intensities corrected for Lorentz and polarization, not for absorption; structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); first *E* map revealed the position of the benzene ring; successive difference Fourier syntheses determined positions of all non-H atoms; structure refined by full-matrix least squares with *RFINE*2 (Finger, 1969); all H atoms located from difference Fourier synthesis; two reflections with $|F_c| \gg |F_o|$ seemed to suffer secondary extinction, excluded in subsequent refinements; final refinement on *F* with anisotropic temperature factors for all non-H atoms and with isotropic H

Table 1. *Final atomic coordinates of the non-*H *atoms* (× 10$^4$) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$*(Å$^2$) |
|---|---|---|---|---|
| C(1) | 3662 (2) | 7671 (2) | 8996 | 4·74 |
| C(2) | 2565 (2) | 8360 (2) | 8792 (4) | 4·85 |
| C(3) | 2731 (3) | 9513 (2) | 8679 (4) | 4·81 |
| C(4) | 3800 (3) | 9936 (2) | 8634 (4) | 5·06 |
| C(5) | 4920 (2) | 9274 (2) | 8791 (4) | 5·07 |
| C(6) | 5412 (3) | 8871 (3) | 7414 (4) | 5·40 |
| C(7) | 4621 (2) | 8076 (2) | 6689 (4) | 4·60 |
| C(8) | 4100 (3) | 7216 (2) | 7636 (4) | 4·98 |
| C(9) | 4633 (2) | 8316 (2) | 9637 (4) | 4·88 |
| C(10) | 5179 (4) | 8073 (3) | 10780 (5) | 6·89 |
| O(11) | 1588 (2) | 7951 (2) | 8715 (4) | 7·53 |
| O(12) | 3713 (1) | 8677 (1) | 6023 (3) | 4·66 |
| C(13) | 3222 (3) | 8171 (2) | 4863 (5) | 5·47 |
| C(14) | 2380 (2) | 8938 (2) | 4205 (4) | 4·26 |
| C(15) | 1593 (3) | 9546 (2) | 4972 (4) | 4·74 |
| C(16) | 835 (3) | 10267 (2) | 4366 (5) | 5·39 |
| C(17) | 826 (3) | 10389 (3) | 3003 (5) | 5·92 |
| C(18) | 1591 (3) | 9801 (3) | 2231 (5) | 6·79 |
| C(19) | 2363 (3) | 9069 (3) | 2823 (4) | 5·61 |

* $B_{eq}$ is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·517 (4) | C(7)—O(12) | 1·426 (4) |
| C(1)—C(8) | 1·538 (4) | C(9)—C(10) | 1·318 (6) |
| C(1)—C(9) | 1·498 (4) | O(12)—C(13) | 1·418 (5) |
| C(2)—C(3) | 1·448 (3) | C(13)—C(14) | 1·492 (4) |
| C(2)—O(11) | 1·216 (3) | C(14)—C(15) | 1·390 (5) |
| C(3)—C(4) | 1·316 (4) | C(14)—C(19) | 1·373 (6) |
| C(4)—C(5) | 1·514 (4) | C(15)—C(16) | 1·373 (5) |
| C(5)—C(6) | 1·551 (6) | C(16)—C(17) | 1·353 (7) |
| C(5)—C(9) | 1·487 (4) | C(17)—C(18) | 1·364 (6) |
| C(6)—C(7) | 1·511 (5) | C(18)—C(19) | 1·386 (5) |
| C(7)—C(8) | 1·534 (5) | | |
| | | | |
| C(2)—C(1)—C(8) | 110·7 (2) | C(1)—C(8)—C(7) | 113·4 (2) |
| C(2)—C(1)—C(9) | 110·5 (2) | C(1)—C(9)—C(5) | 110·5 (3) |
| C(8)—C(1)—C(9) | 109·4 (2) | C(1)—C(9)—C(10) | 125·5 (3) |
| C(1)—C(2)—C(3) | 117·4 (2) | C(5)—C(9)—C(10) | 124·0 (3) |
| C(1)—C(2)—O(11) | 120·8 (2) | C(7)—O(12)—C(13) | 114·9 (2) |
| C(3)—C(2)—O(11) | 121·8 (2) | O(12)—C(13)—C(14) | 108·5 (2) |
| C(2)—C(3)—C(4) | 121·1 (2) | C(13)—C(14)—C(15) | 121·0 (4) |
| C(3)—C(4)—C(5) | 122·9 (2) | C(13)—C(14)—C(19) | 121·0 (3) |
| C(4)—C(5)—C(6) | 112·6 (3) | C(15)—C(14)—C(19) | 117·9 (3) |
| C(4)—C(5)—C(9) | 108·0 (2) | C(14)—C(15)—C(16) | 120·9 (4) |
| C(6)—C(5)—C(9) | 108·1 (2) | C(15)—C(16)—C(17) | 120·6 (3) |
| C(5)—C(6)—C(7) | 114·5 (3) | C(16)—C(17)—C(18) | 119·5 (3) |
| C(6)—C(7)—C(8) | 113·1 (3) | C(17)—C(18)—C(19) | 120·8 (4) |
| C(6)—C(7)—O(12) | 107·5 (2) | C(14)—C(19)—C(18) | 120·2 (3) |
| C(8)—C(7)—O(12) | 111·6 (2) | | |
| | | | |
| C(6)—C(5)—C(9)—C(1) | 64·0 (3) | C(5)—C(9)—C(1)—C(2) | 57·6 (3) |
| C(5)—C(9)—C(1)—C(8) | −64·5 (3) | C(9)—C(1)—C(2)—C(3) | −25·0 (2) |
| C(9)—C(1)—C(8)—C(7) | 52·6 (2) | C(1)—C(2)—C(3)—C(4) | 5·9 (2) |
| C(1)—C(8)—C(7)—C(6) | −42·7 (3) | C(2)—C(3)—C(4)—C(5) | 4·3 (2) |
| C(8)—C(7)—C(6)—C(5) | 43·5 (3) | C(3)—C(4)—C(5)—C(9) | 27·9 (2) |
| C(7)—C(6)—C(5)—C(9) | −53·6 (3) | C(4)—C(5)—C(9)—C(1) | −58·2 (3) |

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* C(7)—H in (1*a*) absorbs at 3·72 p.p.m. as a broad singlet, that in (1*b*) at 3·89 p.p.m. as a triplet of triplets with $J = 10{\cdot}4$ and 5·8 Hz. The results suggested the *anti* relation between the benzyloxy group and the bridge C=O and are in contrast to the case with a *tert*-butyl substituent on the 7 position (Hickmott, Cox & Sim, 1974).

atoms, $R = 0{\cdot}045$, $wR = 0{\cdot}037$, $w = 1/\sigma^2(F_o)$ from counting statistics, $S = 2{\cdot}00$; $(\Delta/\sigma)_{\max} = 0{\cdot}002$; $|\Delta\rho|_{\max}$ in final difference Fourier map $= 0{\cdot}16$ e Å$^{-3}$; all numerical calculations carried out on a Facom M-382 computer in the Science Information Processing Center of the University of Tsukuba; scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic parameters are listed in Table 1.* The molecular structure and numbering scheme are illustrated in the *ORTEP* plot (Johnson, 1976) given in Fig. 1. Bond distances and angles are listed in Table 2. The benzyloxy group was found to be *anti* to the bridge C=CH$_2$ group. Ring *A* which bears the benzyloxy group has a chair conformation, resulting in the substituent being axial. This is consistent with the conformation estimated from the $^1$H NMR spectrum in solution. The bond angles and torsion angles (Table 2) show that ring *A* flattens slightly due to the presence of the axial benzyloxy group. The interatomic distances from O(12) to C(2), C(3) and C(4) are 3·047 (5), 3·029 (5) and 3·017 (5) Å, respectively; all are longer than the estimated values (2·2–2·5 Å) from a Dreiding model. Ring *B* having an α,β-unsaturated carbonyl moiety exists in a half-chair form.

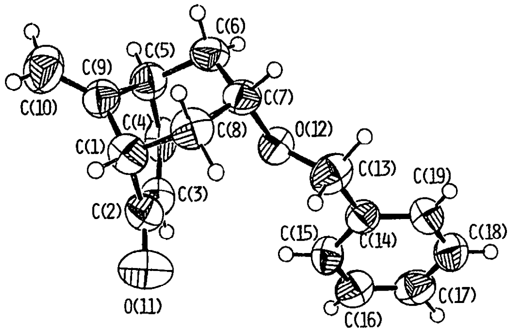

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the molecule with thermal ellipsoids scaled at the 50% probability level and numbering scheme. H atoms are represented by circles of radius 0·1 Å.

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* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43920 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 2-(*p*-Chlorophenyl)-4-phenylindan-1,3-dione

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**Abstract.** C$_{21}$H$_{13}$ClO$_2$, $M_r = 332{\cdot}9$, monoclinic, $P2_1/n$, $a = 8{\cdot}420$ (2), $b = 10{\cdot}913$ (4), $c = 17{\cdot}899$ (3) Å, $\beta = 91{\cdot}79$ (3)°, $V = 1643{\cdot}9$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}338$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}197$ mm$^{-1}$, $F(000) = 688$, $T = 293$ K, $R = 0{\cdot}060$ for 2073 reflexions. The molecule has no unusual bond lengths or angles. There is substantial librational motion of the chlorophenyl ring. The indandione system is twisted out of planarity [maximum deviation from benzene plane 0·253 (3) Å of C atom at 2-position].

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