# Crystal and Molecular Structure of 2-*p*-Bromophenyl-3,4-dimethyl-5-phenyloxazolidine

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D(−)-Ephedrine was allowed to react with *p*-bromophenylbenzaldehyde to give 2-*p*-bromophenyl-3,4-dimethyl-5-phenyloxazolidine. The oxazolidine ring has the 2R:4*S*:5*R* configuration. The crystals belong to the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell. The interatomic distances, bond angles, and a three-dimensional representation are reported.

Aromatic aldehydes react with D(−)-ephedrine to give oxazolidines. This is a stereospecific reaction and a totally induced asymmetric synthesis. Selective degradative studies showed that such oxazolidines have the 2*R*:4*S*:5*R* configuration.[1] In order to confirm this finding, X-ray diffraction studies were conducted on 2-*p*-bromophenyl-3,4-dimethyl-5-phenyloxazolidine, a model compound containing a heavy atom. The results show that while the oxazolidine ring is not quite planar the aromatic group on C-2 is on the opposite side of the ring from the substitutions on C-4 and C-5.

## Experimental Section

*p*-Bromobenzaldehyde (18.5 g, 0.1 mol) and D(−)-ephedrine hydrate (17.4 g, 0.1 mol) were dissolved in absolute alcohol (150 ml), and the solution was heated under reflux for 2 hr on the steam bath. Most of the alcohol was removed under reduced pressure to leave a residue which on cooling gave the crystalline product. The crude product was collected on a filter, pressed dry, and washed with a little ice-cold absolute alcohol, yield 31.5 g (95%). A sample was recrystallized from absolute alcohol twice to give colorless crystals of the product which has a melting point of 87–88°, $[\alpha]^{20}\text{D}$ −65.8° (*c* 2, absolute alcohol).

*Anal.* Calcd for $C_{17}H_{18}BrNO$: C, 61.49; H, 5.42; N, 4.22; Br, 24.10. Found: C, 61.23; H, 5.53; N, 4.31; Br, 24.71.

The product crystallizes from isopropyl alcohol, benzene, ether, and ethyl alcohol as flakes. However, by seeding an alcoholic solution and repeated heating and cooling, well-defined crystals were obtained which were used for the X-ray diffraction studies.

**Structure Determination.**—2-*p*-Bromophenyl-3,4-dimethy-5-phenyloxazolidine crystals belong to the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell with dimensions of $a$ = 17.85 (2) Å, $b$ = 8.04 (1) Å, and $c$ = 10.97 (1) Å. The calculated density is 1.40 g/cm$^3$, as compared with a density of 1.36 (2) g/cm$^3$ observed by flotation in $ZnCl_2$ solution. A total of 1219 reflections above background were collected around the $c$ axis of a crystal approximately 0.35 × 0.40 × 0.50 mm on a semiautomatic linear diffractometer with Mo K$\alpha$ radiation and a graphite monochromator to a maximum $\theta$ of 21°. For each reflection $\omega$ was scanned at 1.0 deg/min through 1.5–2.1° with 10-sec. background counts on each side. The linear absorption coefficient for this crystal is 27.9 cm$^{-1}$ for Mo K$\alpha$ radiation.[2a] The data were corrected for Lorentz and polarization effects. Because of the somewhat irregular edges of the crystal, no correction was made for absorption.

The Harker peaks of an $E^2 - 1$ synthesis yielded the bromine positions, and subsequent Fourier maps led to positions of all the nonhydrogen atoms. The atomic scattering factors were taken from Hanson, *et al.*,[3] with dispersion corrections for Br taken from the International Tables.[2b] Full-matrix least-squares refinement with SORFLS[4] was employed in which positional parameters for all 20 nonhydrogen atoms, anisotropic thermal parameters for the bromine atom, and isotropic thermal parameters for the other atoms were varied. A plot of $\sqrt{\Sigma_n(F_o - F_c)^2/n}$ in intervals of $F_o$ near the end of the refinement led to the following weighting scheme

$$F_o < 12.28 \qquad \sigma = -0.040F_o + 1.56$$

$$F_o \geq 12.28 \qquad \sigma = 0.016F_o + 0.873$$

where $\sigma = 1/\sqrt{w}$.

Refinement was continued with each of the enantiomers of this optically active compound. The final weighted residual

$$R_w = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

index indicated the correct enantiomer with an $R_w$ of 8.61% as compared with an $R_W$ of 9.90% for the other enantiomer. A statistical test[5] based on the ratio of the two residual indices indicated that the correct enantiomer was known with a probable error of less than 0.5%.[6]

The interatomic distances and bond angles with errors as calculated by SORFFE[7] are listed in Table II[6] and three-dimensional representations drawn by the local version of ORTEP[8] are given in Figures 1a and b. The variation in the bond distances within the phenyl group indicates that the true error is at least twice that calculated by SORFFE. See p 2262.

The molecules appear to be held together in the crystal only by van der Waals interactions. Figure 1a shows the molecule as viewed along an axis almost parallel to the $a$ axis. The other three molecules in the unit cell pack behind this one in about 4.4-Å intervals along the $a$ axis with orientations dictated by the screw axes.

Figure 1b shows the aromatic group on C-2 to be on the opposite side of the five-membered ring from the methyl group on C-4 and the aromatic group on C-5. In Table III[6] are listed the distances of the ring and its attached atoms from the best (least-squares) plane through the five-membered ring.

**Registry No.**—2-*p*-Bromophenyl-3,4-dimethyl-5-phenyloxazolidine (2*R*:4*S*:5*R*), 29863-93-2.

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(5) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(6) A listing of final positional and thermal parameters and observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(7) Local version of ORFFE: W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-306, Oak Ridge National Lboratory, Oak Ridge, Tenn., 1964.

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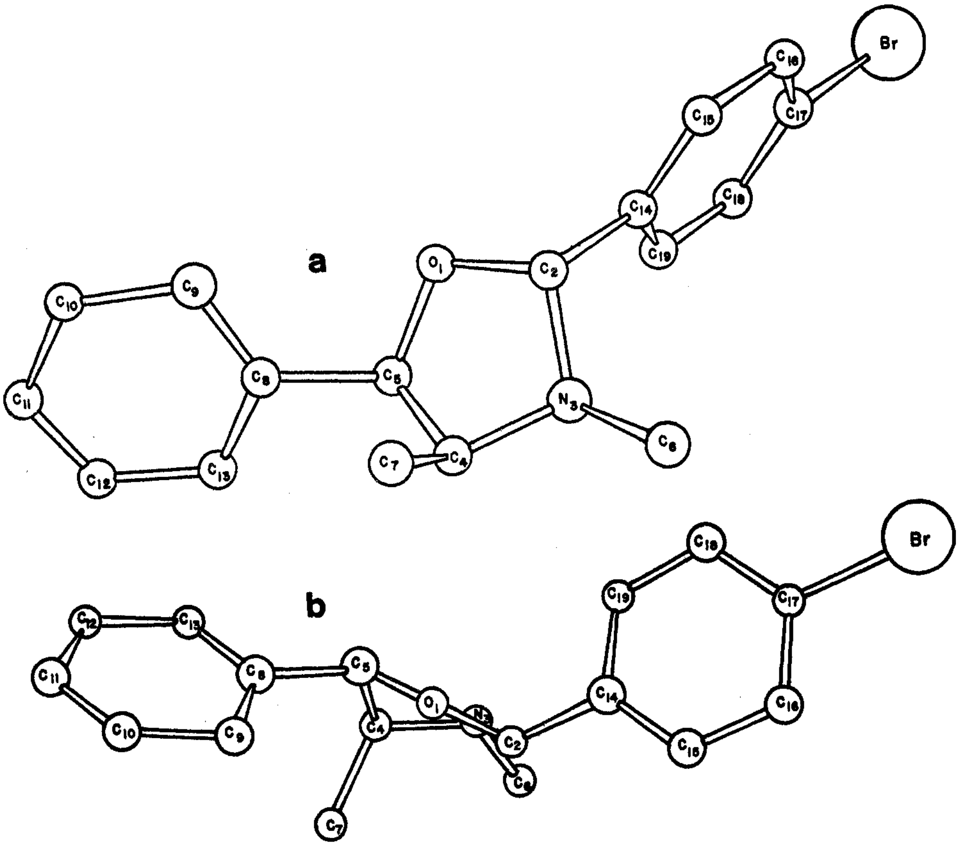

Figure 1.

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# Some Properties of Triarylimidazolyl Radicals and Their Dimers

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The electronic spectra of 2,4,5-triarylimidazolyl radicals 1 are strongly influenced by substitution on phenyl rings; spectra of dimers 2 are not. The rates of disappearance of 1 in benzene at 27° vary over 100-fold with substitution of phenyl rings. Any ortho substituent in Ar increases the rate constant relative to position isomers, a fact consistent with radical destabilization by ortho substituents through steric disruption or ring coplanarity.

Colored triarylimidazolyl free radicals 1 are formed from the thermal or photolytic dissociation of hexaarylbiimidazoles, the oxidation products of triarylimidazoles 4.[2] Two hexaarylbiimidazole isomers have been reported.[3] In solution, the more stable 2 is produced at room temperature and 3 is formed below −20°. Interconversion of 2 and 3 involves 1. Structures were inferred from infrared data.[3] Dimer 2 is referred to by some authors as the photochromic dimer and 3 as the thermochromic dimer. The kinetics of radical recombination have been reported to be second order in radical concentration.[2c,d] Longer reaction times reveal deviation from second-order kinetics. Wilks and Willis reported 3/2 order which, after several half-lives, changed to first-order kinetics in radical disappearance.[4]

We have prepared some new hexaarylbiimidazoles, particularly a group bearing ortho substituents in the aromatic rings, and report here the effect of substitution on the rate of radical disappearance and on spectra of

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(1) To whom inquiries should be addressed.

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