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STRUCTURE AND STEREOCHEMISTRY OF ISOMERIC 3,3'-di-(*p*-BROMOPHENYL)-bi-3-PHTHALIDYLS

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We wish to report that a crystal structure determination by three dimensional X-ray analysis of the title compound A, m.p. 262-3° has revealed that it is the *meso* isomer. By implication the isomer B, m.p. 226-8° is racemic (1).

A variety of reducing agents like hydroiodic acid, zinc and hydrochloric acid, aluminium and sulphuric acid convert *o*-benzoylbenzoic acids [I] to isomeric mixture of dilactones [II] (2 to 7). Only in a single instance i.e., [I, 4'R=H] has separation of these isomers been attempted (6).

We obtained a mixture of biphthalidyls in quantitative yield by reaction of a solution of sodium iodide in acetone with III [4'R = Br]. The product was separated into

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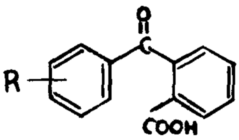
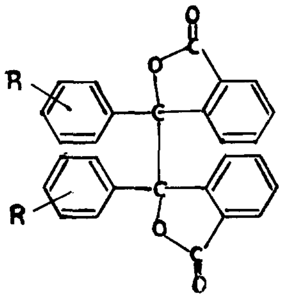


I



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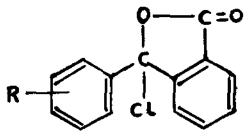

III

components A, m.p. 262-3° and B, m.p. 226-8° by fractional crystallization. Quantitative estimation of the mixture by IR spectroscopy revealed that product consisted of a 70:30 ± 2% mixture, with A predominating. The preferential formation of one of the isomers is of mechanistic significance in the formation and combination of radicals, and stereoelectronic factors involved thereof.

As part of this study, we have now examined the structure of the more abundant and higher melting isomer A. This substance crystallizes in the triclinic system with cell parameters $\underline{a}$ = 7·98 Å, $\underline{b}$ = 8·08 Å, $\underline{c}$ = 9.66 Å, $\underline{\alpha}$ = 85·4°, $\underline{\beta}$ = 98·4°, $\underline{\gamma}$ = 104·7° and one molecule in the unit cell. Intensity data were collected for the $\underline{h}\,0\,\underline{\ell}$, $0\,\underline{k}\,\underline{\ell}$ and $\underline{h}\,\underline{k}\,\underline{\ell}$ [$\underline{\ell}$ = 0 to 8] zones using the Weissenberg technique. Intensities of 932 observable reflections were estimated visually.

The structure analysis was commenced assuming that the space group was centrosymmetric P $\bar{1}$. The convergence of the structure in this space group to a final R-index of 0·096 confirms this assumption and leads to the conclusion that the substance taken up for study is the *meso* isomer existing in the staggered configuration.

The coordinates of bromine atom were derived from (*h k* 0) (*h* 0 *ℓ*) Patterson syntheses. The structure was solved in projections by the heavy atom technique and then refined by least square methods using three dimensional data. All the atoms were given anisotropic temperature factors. The final three dimensional electron density distribution is shown in FIG.1 by means of superimposed contour sections drawn perpendicular to *b* axis. The atomic arrangement is also shown. The analysis confirms two well-known characteristics of the lactone group, *viz*. shortening of the C-O bond adjacent to the C=O bond and planarity of the group (8).

There are no physical methods of general validity for distinguishing between *meso* and racemic isomers (9). The interesting differences in the IR spectra* of the isomers A and B and differences in the symmetry of their structures, have encouraged us to look for a method based on spectroscopic consequences of molecular symmetry. In principle a method based on mutual exclusion rule for the Raman and IR spectra of centrosymmetric structures should be available when there is free rotation around the central bond joining the two halves of the meso and racemic molecules. We are now engaged in testing the

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* IR spectra were taken in nujol mull.

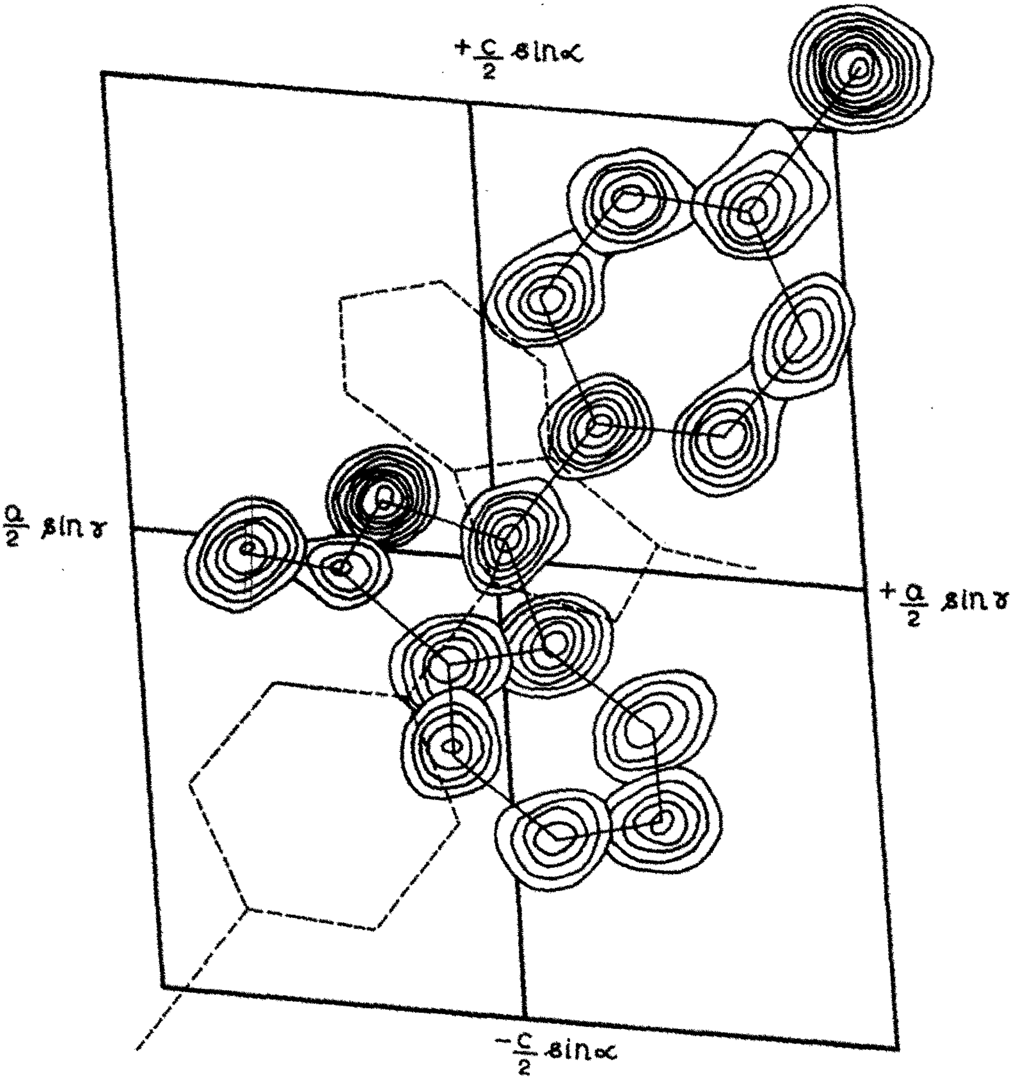
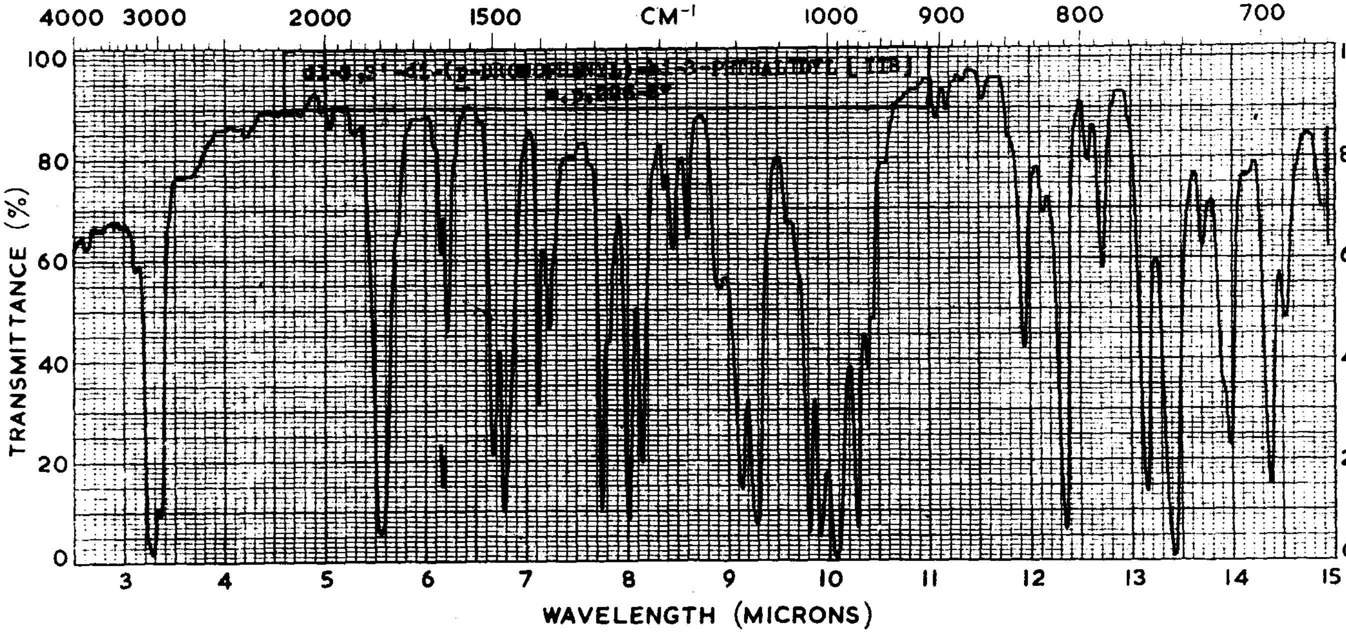


FIG.1. Final three-dimensional electron density map. Superimposed contour sections are drawn perpendicular to **b** axis. For clarity only contours corresponding to one half of the molecule are drawn.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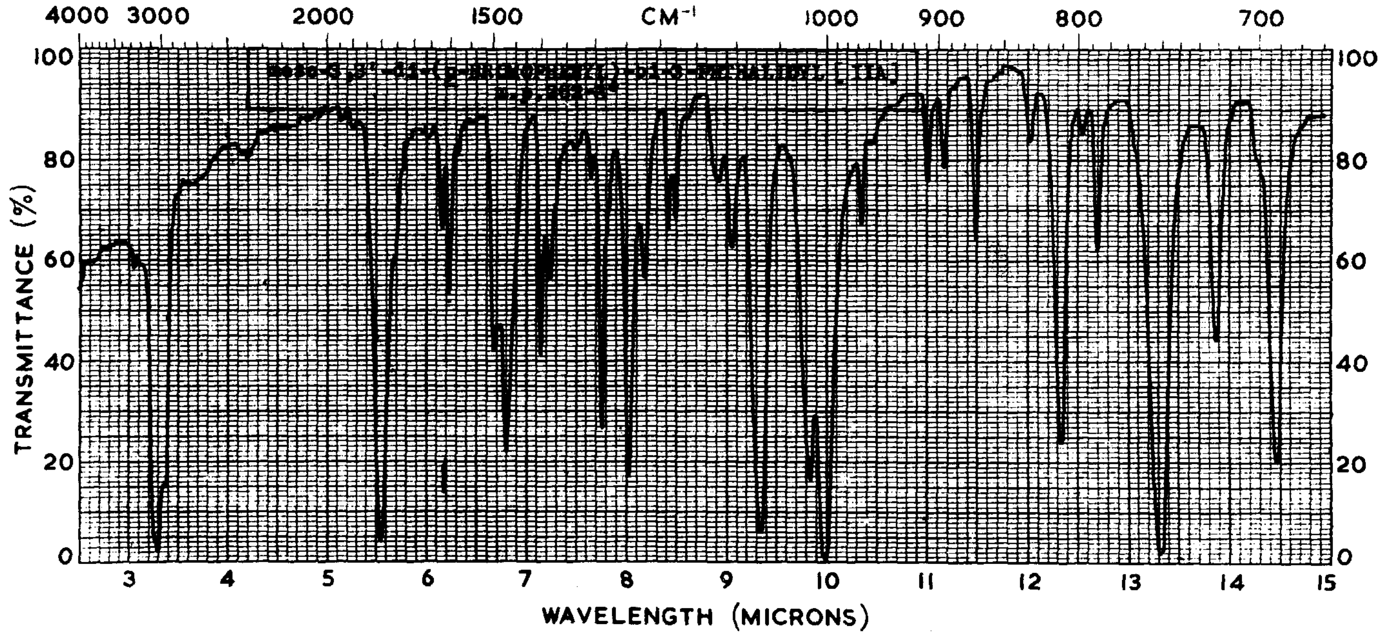
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possibility of such a method. We are also attempting to resolve the racemic mixture B into antipodes through suitable derivatives.

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