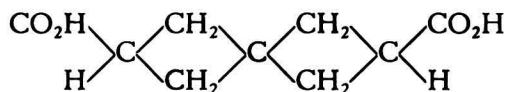


Chemistry. — *Optical resolution of a spirocyclic compound of the allene type.* By H. J. BACKER and H. B. J. SCHURINK. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of April 28, 1928).

Recent publications ¹⁾ on spirocyclic compounds of the asymmetric allene type $xyC : C : Cxy$ induce us to publish some results of our investigations in this field.

In order to test the stereochemical theory, that such spiranes should exist in enantiomorphs, we have studied *spiroheptanedicarboxylic acid* :



FECHT ²⁾ has obtained this acid in small yield, starting from tetrabromopentaerythritol and malonic ester.

After having improved the preparation until the yield was about 80 %, we attempted the resolution by means of the dibrucine salt, which crystallises with six molecules of water in short prisms and decomposes at about 135°.

This brucine salt, recrystallised carefully from water and decomposed by ammonia, gives an optically active ammonium salt. The rotation is feeble and reaches its maximum value after about 5 crystallisations.

The rotatory power is given in the following table for different wave lengths.

Rotatory dispersion of ammonium spiroheptanedicarboxylate.

$\lambda(\mu\mu)$	656.3 (C)	589.5 (D)	546.3 (Hg)	486.1 (F)
$[\alpha]$	+ 0°.11	0°.13	0°.15	0°.19
$[M]$	+ 1°.9	2°.3	2°.6	3°.4

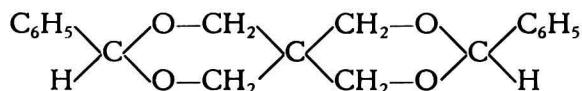
The free acid being only little soluble in water cannot be studied accurately in aqueous solution. Its ethereal solution shows a positive rotation: $[M]_D = +1°.9$.

We believe that this is the first observation of an optically active spirane of this type, whose resolution is completely reproducible.

¹⁾ PFEIFFER and BACKES, Ber. 61, 434 (1928); BÖESEKEN and FELIX, Ber. 61, 787 (1928).

²⁾ Ber. 40, 3888 (1907).

Further we studied a compound of analogous structure, the *dibenzal-pentaerythritol* :



READ ¹⁾ has sought already in 1912 for optical activity in the case of this and related compounds.

BÖESEKEN and FELIX ²⁾ publish to have observed for this compound on one occasion an optical activity, which could not be reproduced.

Our results, already obtained in 1927, may be shortly summarized.

The dibenzal compound, prepared under different conditions, had always the same melting point (162°) and the same chemical properties. Thus the occurrence of a cis-trans isomerism, which might be possible in the case of a pyramidal distribution of the valences of the central carbon atom, is improbable.

The substance was obtained in large hexagonal crystals with edges up to half an inch in length.

The Röntgen analysis, made in the inorganic chemical laboratory by Mr. VAN MELLE, showed that the crystal has a three-fold screw axis, perpendicular to the basal plane. Thus dextro- and laevorotatory crystals should be possible.

Indeed both kinds of crystals were obtained. The rotation could not be measured accurately with our polarisation apparatus; the value is about $\alpha_D = \pm 2^\circ/\text{mm}$.

The Röntgen analysis of dibenzal-pentaerythritol, the results of which will be published elsewhere, has proved, that the molecules in the crystal possess three mutually perpendicular two-fold axes, according to the symmetry of an orthorhombic bisphenoïde. Thus the central carbon atom has a tetrahedral (not a pyramidal) distribution of its valences and the phenyl groups must be placed in the long axis of the molecule, for instance :



The optical activity of the crystals is caused by the asymmetric distribution of the molecules.

None of the crystals, when dissolved in alcohol, ethyl acetate or chloroform, has shown a trace of optical activity.

Groningen, April 1928.

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¹⁾ J. chem. Soc. **101**, 2090 (1912).

²⁾ Loc. cit.