



Absolute structure

H. D. Flack

Basel, 1st September 2016



**UNIVERSITÉ
DE GENÈVE**
FACULTÉ DES SCIENCES



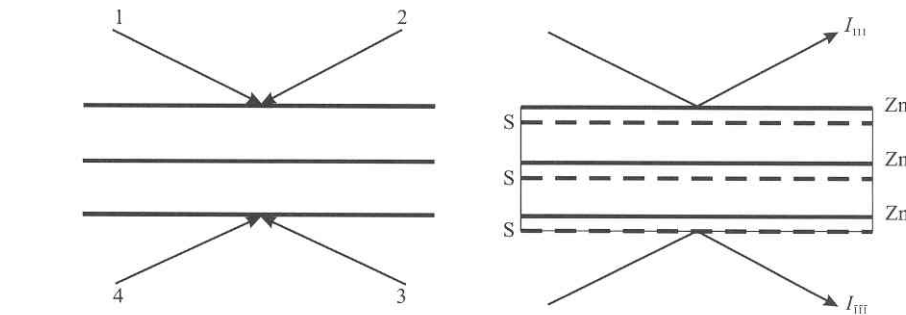
Friedel, G. (1913).

Loi générale de la diffraction des rayons
Röntgen par les cristaux.

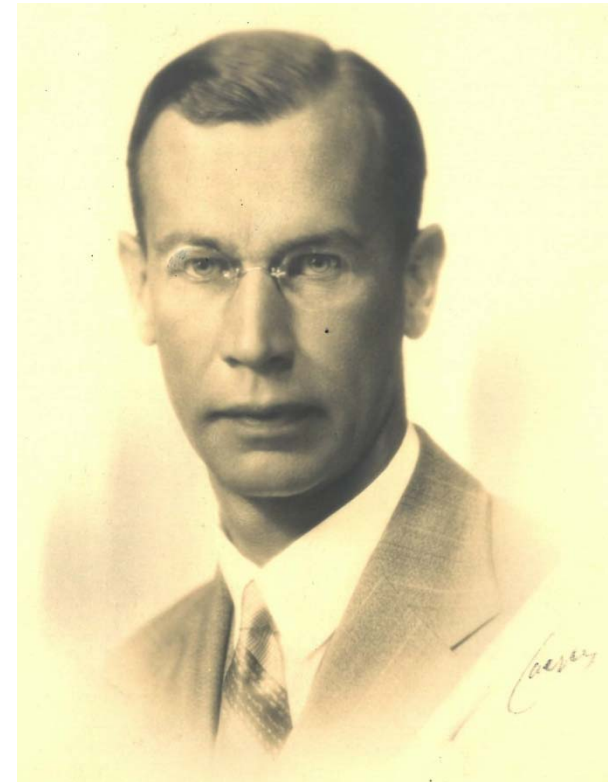
C. R. Acad. Sci. Paris **156**, 1676-1679.



Georges Friedel



Waller, I. (1928).
Über eine verallgemeinerte Streuungsformel.
Zeit. Phys. **51**, 213-231.



Ivar Waller

$$f_j^0 + f_j' + i f_j''$$

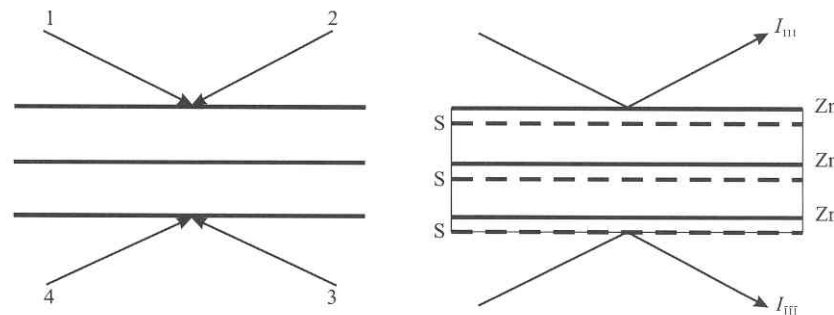


Figur 1. Den unge Ivar Waller träget studerande vid sitt skrivbord i Göteborg.

Coster, D., Knol, K. S. and Prins, J. A. (1930).
Unterschiede in der Intensität des
Röntgenstrahlen-reflexion an den beiden 111-
Flächen der Zinkblende.
Z. Phys. **63**, 345-369.



Dirk Coster



1951
-272
(Reprinted from *Nature*, Vol. 168, p. 271, August 18, 1951)

DETERMINATION OF THE ABSOLUTE CONFIGURATION OF OPTICALLY ACTIVE COMPOUNDS BY MEANS OF X-RAYS

By PROF. J. M. BIJVOET, A. F. PEERDEMAN

AND

A. J. van BOMMEL

van 't Hoff Laboratory, University of Utrecht

J. H. VAN 'T HOFF extended the structural formulæ of organic chemistry to include spatial configuration ("La chimie dans l'espace" (1874), the aliphatic carbon atom with hydrogen or other atoms at the corners of a tetrahedron surrounding it). X-ray analysis has determined the exact configurations and the interatomic distances accurately to within a hundredth of an angstrom unit.

Optically active compounds are not superimposable and are the inverted image of each other. Now it is a remarkable fact that while all details of such configurations can be determined, it yet remained unsolved, whether model or inversion corresponds with a given—say the dextrorotatory—compound. Our present investigation was concerned with this question.

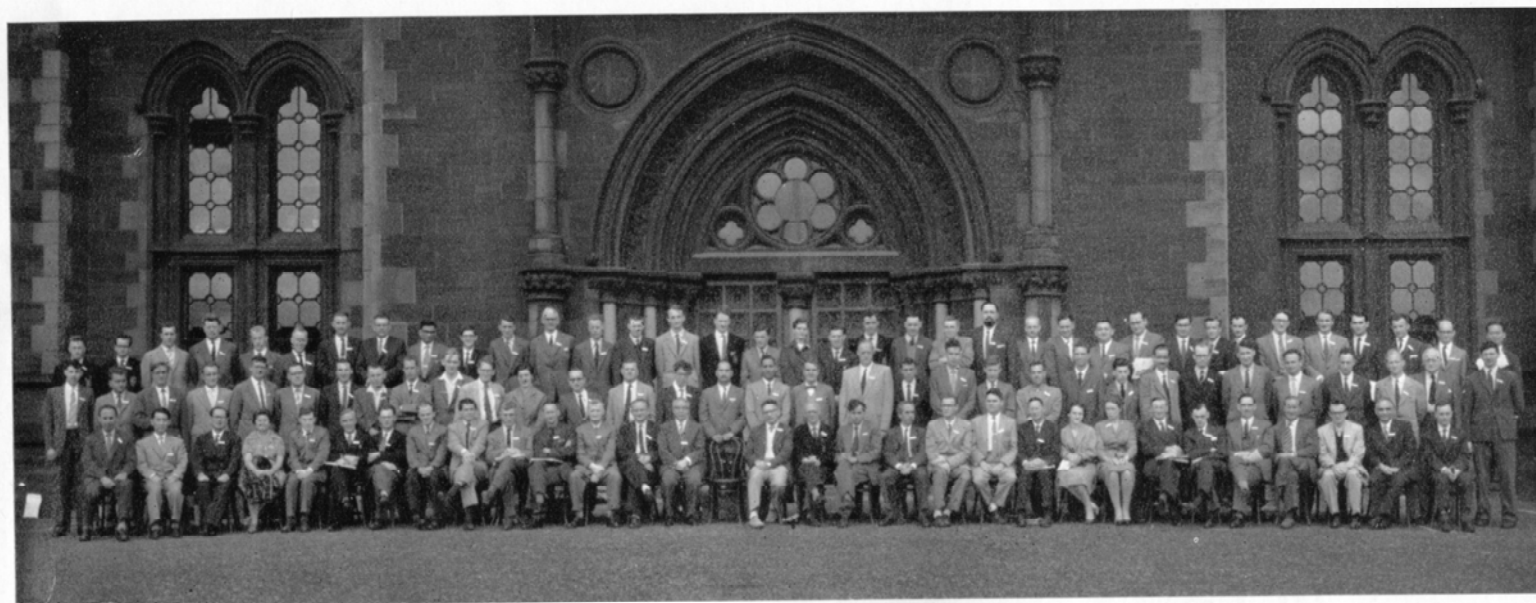
It is impossible to determine absolute configurations by chemical means, which show only the relationship between different structures. These relationships would not alter in any respect if every optically active compound should possess its inverted configuration. Absolute configurations—introduced for the sake of expressing relationship—were based on mere convention. Emil Fischer attributed the configuration of Fig. 2b to natural, dextrorotatory, tartaric acid—with an even chance that this choice would fit the real situation.

Of the physical methods of determining absolute configuration, the theoretical calculation of the rotatory power is the most obvious and that most studied; hitherto, the results, however, have lacked conclusiveness. Recently, a discussion of the relation between crystal structure and face development has been put forward. As to the X-ray method, X-rays are not supposed to be able to determine absolute configuration as they measure the interatomic distances, which do not differ for model and inversion.

This condition may be illustrated by the simple



Johannes Martin Bijvoet



CONFERENCE ON COMPUTING METHODS AND THE PHASE PROBLEM IN X-RAY CRYSTAL ANALYSIS, Glasgow, August 10-12, 1960

CONFERENCE PHOTOGRAPH

FRONT ROW (*left to right*)—H. Schemmel, Y. Iitaka, R. Sadanaga, K. Dornberger-Schiff, G. Walker, C. H. Carlisle, T. Hamor, G. A. Sim, P. Pauling, J. D. Dunitz, S. McGavin, J. Iball, V. Vand, I. Nitta, (J. M. Robertson), R. Pepinsky, J. C. Speakman, D. W. J. Cruickshank, W. Cochran, W. N. Lipscomb, H. Hauptman, E. F. Bertaut, O. Kennard, J. M. Rowe, P. G. Owston, B. Richards, D. Rogers, W. A. Pillow, R. A. Sparks, H. A. Levy, A. Dennery.

MIDDLE ROW (*left to right*)—J. S. Wood, E. Hoehne, I. Olovsson, B. Matković, R. Dickerson, H. Jaggi, R. E. Rund'e, D. P. Shoemaker, D. van der Helm, A. Åkeson, G. S. D. King, H. Muirhead, J. Ladell, F. H. Herbststein, M. G. Rossmann, G. Kartha, F. R. Ahmed, G. A. Jeffrey, H. Sörum, R. K. McMullan, I. Murray, M. Wells, A. Zalkin, P. Sutton, P. Tollin, J. Leech, J. S. Rollett, O. S. Mills, S. Šćavničar, A. Niggli, T. Löfgren, C. J. Brown, M. Woolfson.

BACK ROW (*left to right*)—A. T. McPhail, I. C. Paul, S. Bähr, W. Hoppe, R. Liminga, D. Feil, L. H. Jensen, E. C. Lingafelter, H. N. Shrivastava, C. L. Coulter, D. M. Blow, T. S. Wylie, B. Strandberg, S. Westman, S. Åsbrink, J. G. Sime, D. G. Watson, S. Sutherland, J. Trotter, G. Ferguson, W. Fuller, S. Arnott, J. L. Katz, D. A. Marvin, D. F. Grant, F. A. Kanda, H. Brumberger, J. S. Clunie, A. W. Davie, E. L. Drever, J. M. Cowley, B. Dawson, J. Wunderlich, G. Will, S. C. Abrahams, Y. Okaya.

Rogers, D. (1981).

On the application of Hamilton's ratio test to the assignment of absolute configuration and an alternative test.

Acta Cryst. **A37**, 734-741.

$$f^o_j + f^{'_j} + i \eta f^{''_j}$$

Flack, H. D. (1983).
On Enantiomorph-Polarity Estimation.
Acta Cryst. A **39**, 876-881.



$$G(hkl) = (1 - x) |F(h \ k \ l)|^2 + x |F(\bar{h} \ \bar{k} \ \bar{l})|^2$$

$$C = (1 - x) X + x \bar{X}$$

Jones, P. G. (1984).

The determination of absolute structure. I.

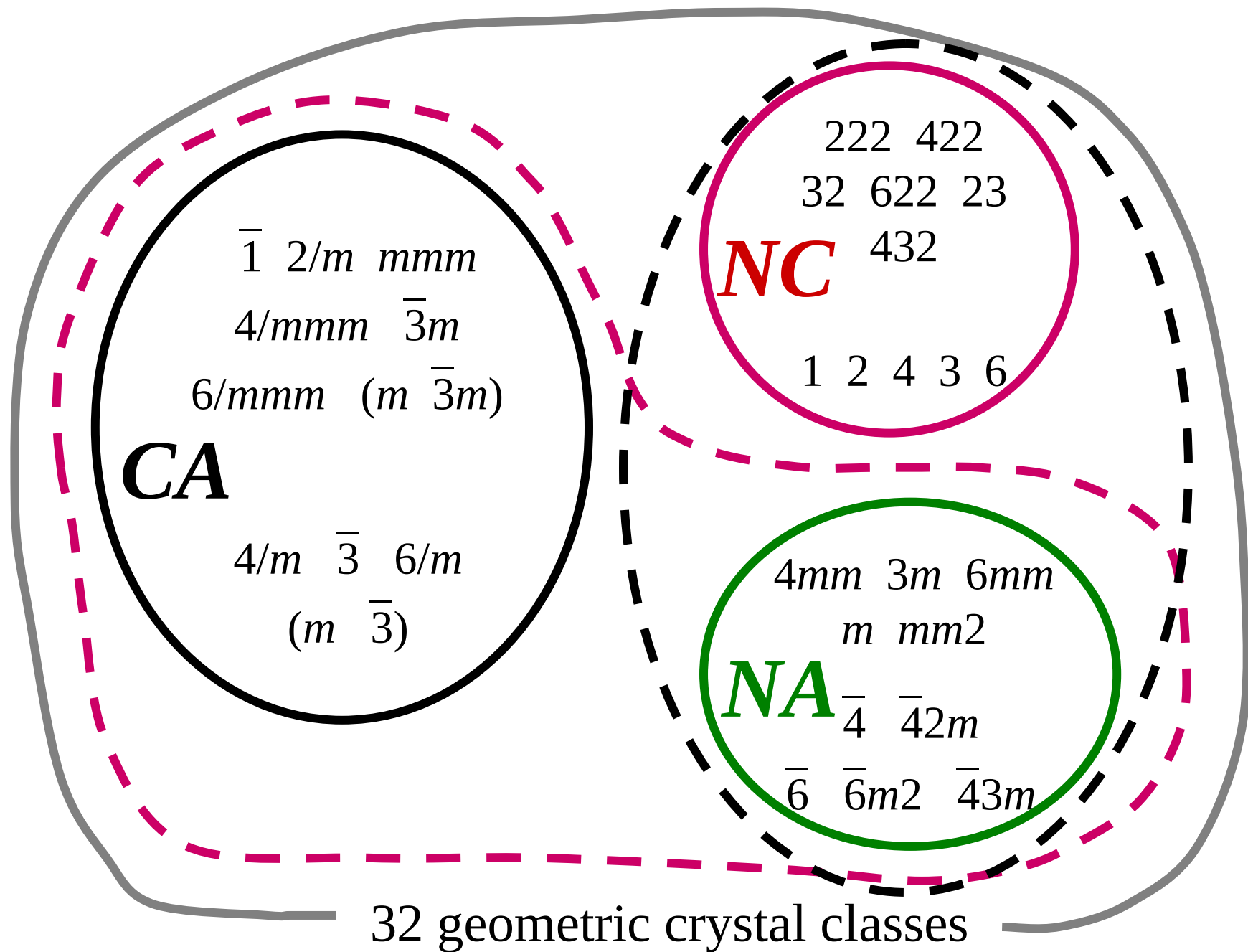
Some experiences with the Rogers η refinement.

*Acta Cryst. A***40**, 660-662.



Peter Jones

The use of the general term 'absolute structure' (to signify a structure successfully distinguished from its inverse by, for example, analysis of anomalous scattering effects) is recommended.







Claude Piguet Gérald Bernardinelli Jiri Mareda



David Watkin Howard Flack Jussi Kivikoski

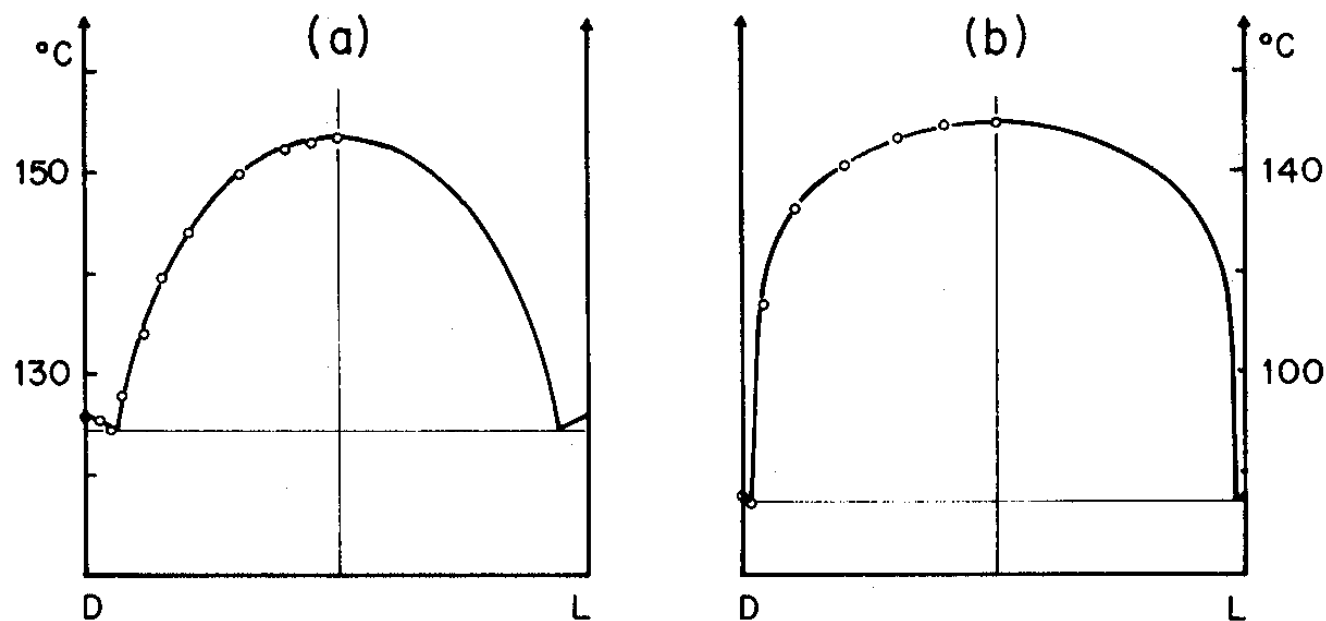


Figure 1 Melting point diagrams of α -(1-naphthoxy)propionic acid² (a) and α -(1-naphthyl)propionic acid³ (b). Experimental points are indicated by circles. The liquidus curves shown were calculated by means of the Prigogine-Defay equation (Section 2.3.2).

α -(1-naphthoxy) propionic acid & α -(1-naphthyl) propionic acid

Separatum
HELVETICA CHIMICA ACTA
Vol. 65, Fasc. 3, p. 924–933 (1982)

für Dr. Flück mit freundlichen Grüßen
W. Oberhänsli

**86. Die spontane Spaltung von 3,3-Diäthyl-5-methylpiperidin-2,4-dion
(Methypylon) in die optischen Isomeren. Eine Röntgenstrukturanalyse eines
isodimorphen Systems von Mischkristallen**

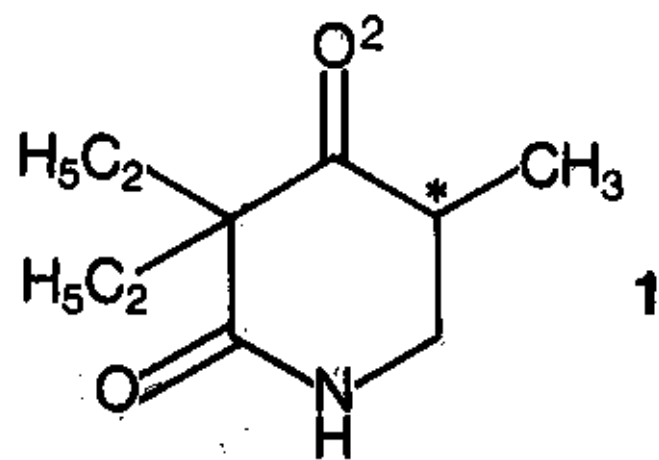
von Willi E. Oberhänsli

Zentrale Forschungseinheiten der *F. Hoffmann-La Roche & Co. AG*, CH-4002 Basel

Herrn Professor Dr. *Walter Boguth* zum 65. Geburtstag gewidmet

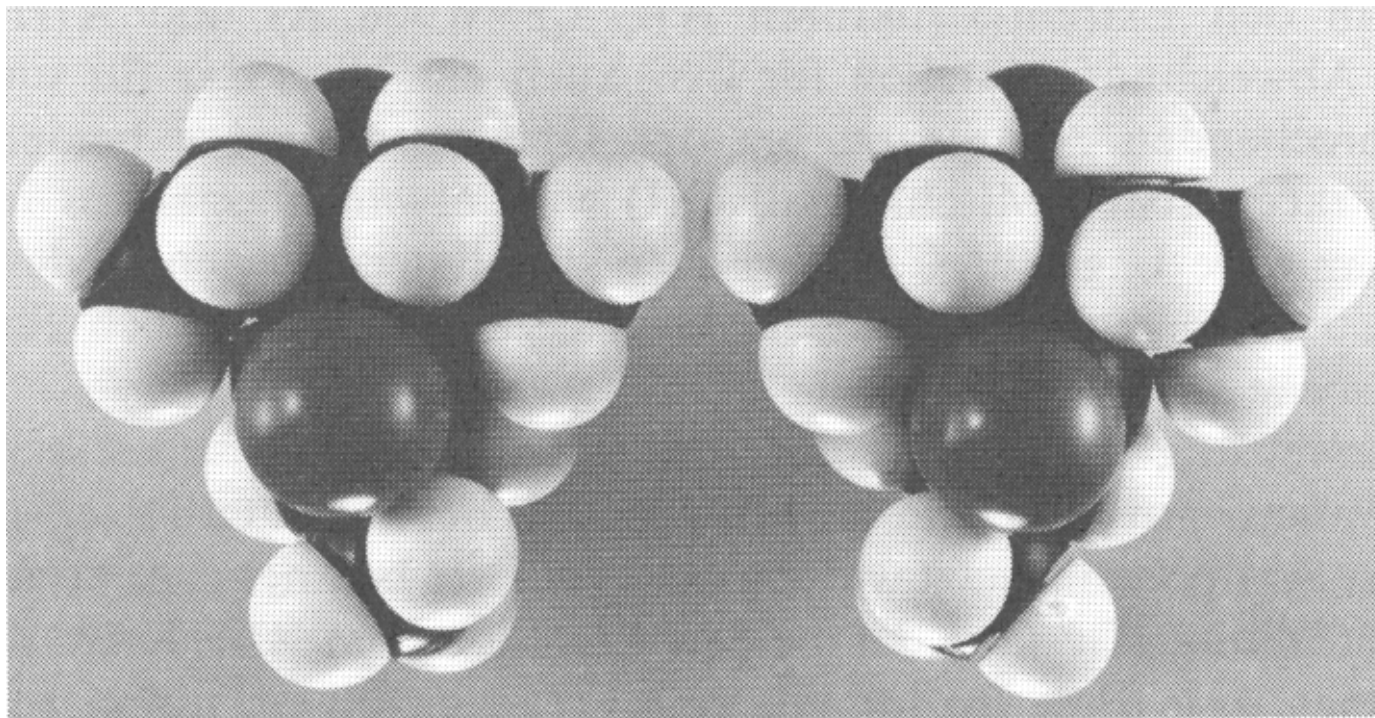
(17.II.82)

**The Spontaneous Resolution of the 3,3-Diethyl-5-methylpiperidine-2,4-dione (Methypylon) into its
Optical Isomers. An X-Ray Structure Analysis of an Isodimorphous System of Mixed Crystals**

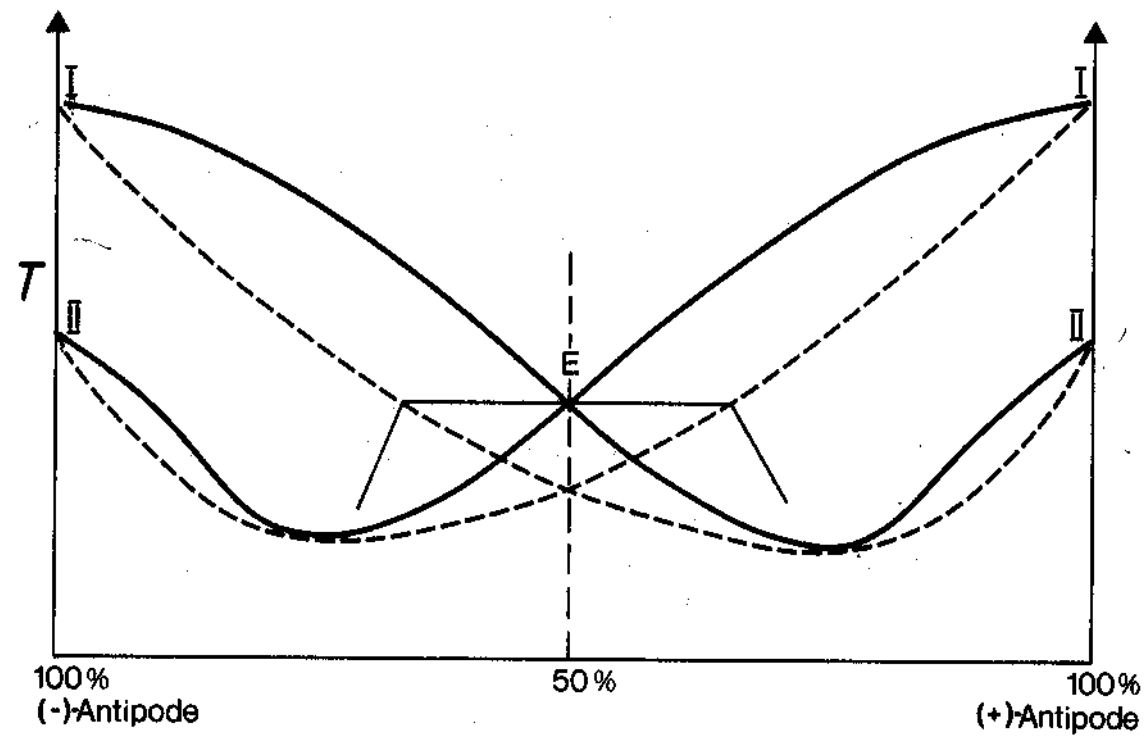


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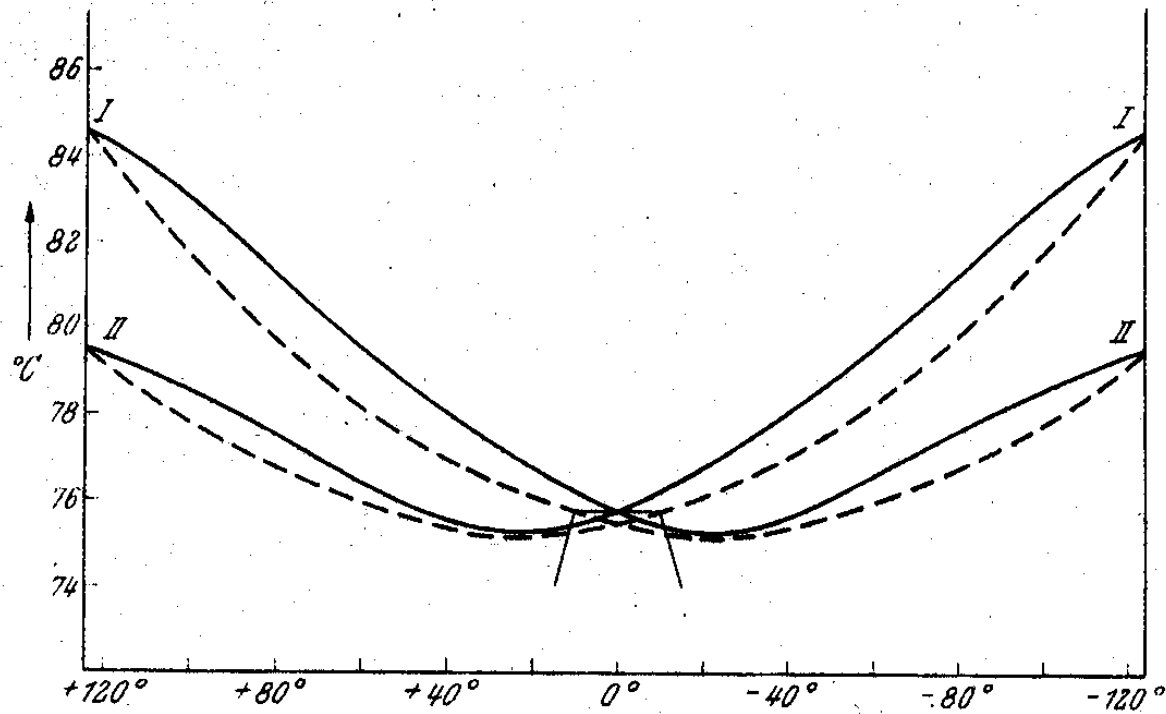
Methyprylon



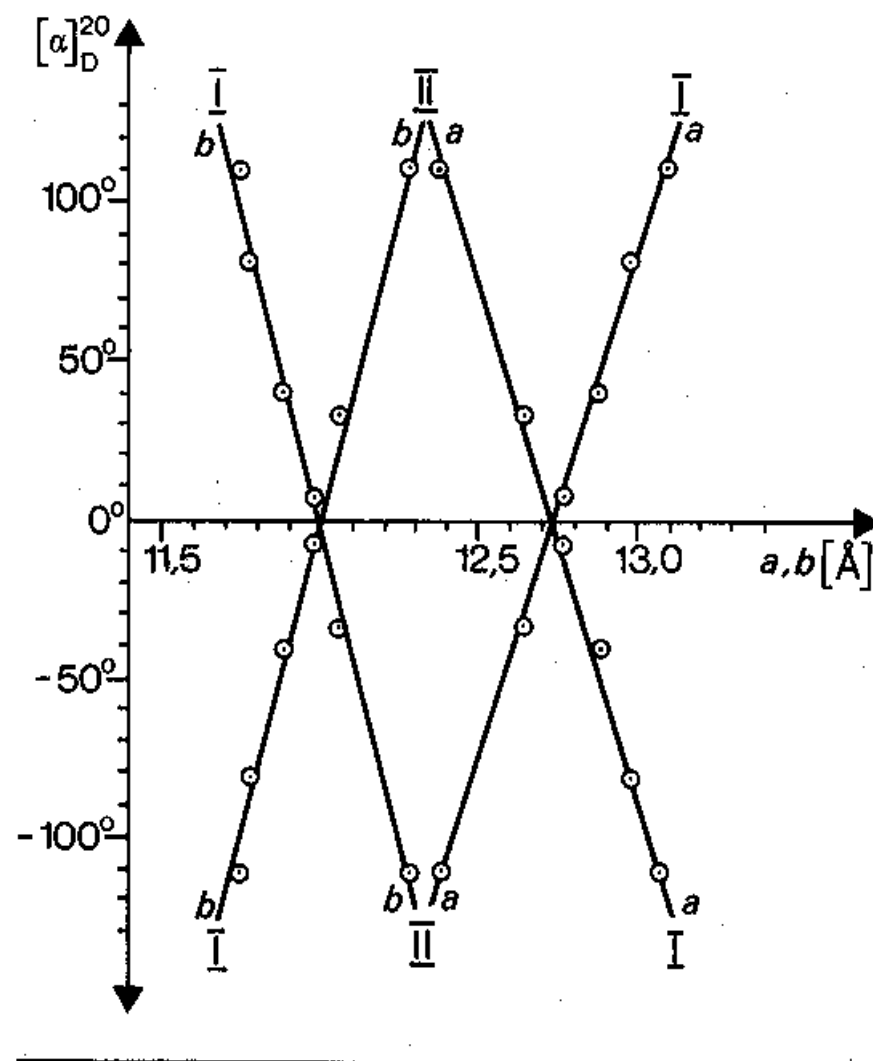
Methyprylon 3D



Crossing isodimorphism with two minima



Melting point diagram of methyprylon



Methypylon cell dimensions and optical activity



The End



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Absolute configuration and absolute structure

Absolute configuration: The spatial arrangement of the atoms of a physically-identified chiral molecular entity (or group) and its stereochemical description (*e.g.* *R* or *S*, *P* or *M*, *D* or *L*, *etc*).

Absolute structure: The spatial arrangement of the atoms of a physically-identified non-centrosymmetric crystal and its description by way of unit-cell dimensions, space group and representative coordinates of all atoms.