

THE ABSOLUTE CONFIGURATION OF 1S,5S-(-)-ARGEMONINE
AND OF 1R,3R-(+)-TRÖGER'S BASE.

S. F. Mason, K. Schofield, R. J. Wells, J. S. Whitehurst, and G. W. Vane.
School of Chemical Sciences, University of East Anglia, Norwich, (S.F.M.
and G.W.V.), and Chemistry Department, University of Exeter, (K.S., R.J.W.
and J.S.W.).

(Received 7 November 1966)

In a recent communication (1) it is reported, from an empirical comparison of the respective optical rotatory dispersion curves, that (+)-Tröger's base (2) and (-) argemonine (3,4) have the same absolute configuration (1S,5S). This particular comparison illustrates the shortcomings inherent in the empirical comparison of Cotton-effect curves, for a non-empirical analysis of the circular dichroism spectra of these isomers at 80°K (Fig. 1), where the more-stable folded conformations (I) and (II) are predominant, shows that, whilst (-)-argemonine has indeed the (1S,5S)-configuration (II), the (+)-isomer of 1,2'-methylene-3-p-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (Tröger's base) has the (1R,3R)-configuration (I).

The method of analysis, based upon the exciton theory of the optical rotatory power of dimeric systems, has been described (5) for the case of calycanthine which, like Tröger's base, consists optically of two non-coplanar aniline chromophores. The optical properties of argemonine arise similarly from couplings between the transition dipoles of the two non-coplanar veratrole chromophores. In dimeric systems with a two-fold symmetry axis there are two coupling modes for each electronic transition

of the constituent monomer, one with A and the other with B symmetry in the group C_2 of the dimer molecule. The two coupling modes give rise to two circular dichroism bands with opposite sign, as is observed in the region of the long-wavelength absorption band of both argemonine and Tröger's base (Fig. 1).

Whether the circular dichroism band due to the A or the B coupling mode is positive or negative, or lies at the longer or the shorter wavelength, is determined by the stereochemistry of the dimeric molecule and by the orientation of the transition dipole moment in each monomer chromophore. The overall stereochemistry of Tröger's base is similar to that of argemonine, but the orientation of the transition dipole responsible for the long wavelength absorption band is different in the respective monomer chromophores. The transition moment of lowest frequency in aniline is directed in the molecular plane perpendicular to the two-fold symmetry axis of the chromophore, whereas the corresponding transition dipole of veratrole is orientated along the two-fold axis of the chromophore (6).

Calculations of the rotational strengths of argemonine and Tröger's base, based upon the above orientations of the monomer transition moments, and the distance and angles between the two monomer moments in the respective dimeric systems, show that the circular dichroism band due to the A coupling mode is positive and that due to the B mode is negative for the (1S,5S)-configuration of argemonine and the analogous (1S,3S)-configuration of Tröger's base. However, the calculated frequencies lie in a converse order in the two cases. The circular dichroism band due to the B coupling mode lies at a longer wavelength than that due A coupling mode in argemonine, whereas in Tröger's base it is the dichroism band due to the A coupling mode which lies at the longer wavelength. Owing to the different orientations of the low-frequency transition moment in the aniline and in the veratrole chromophore, the A coupling mode has the lower energy in Tröger's

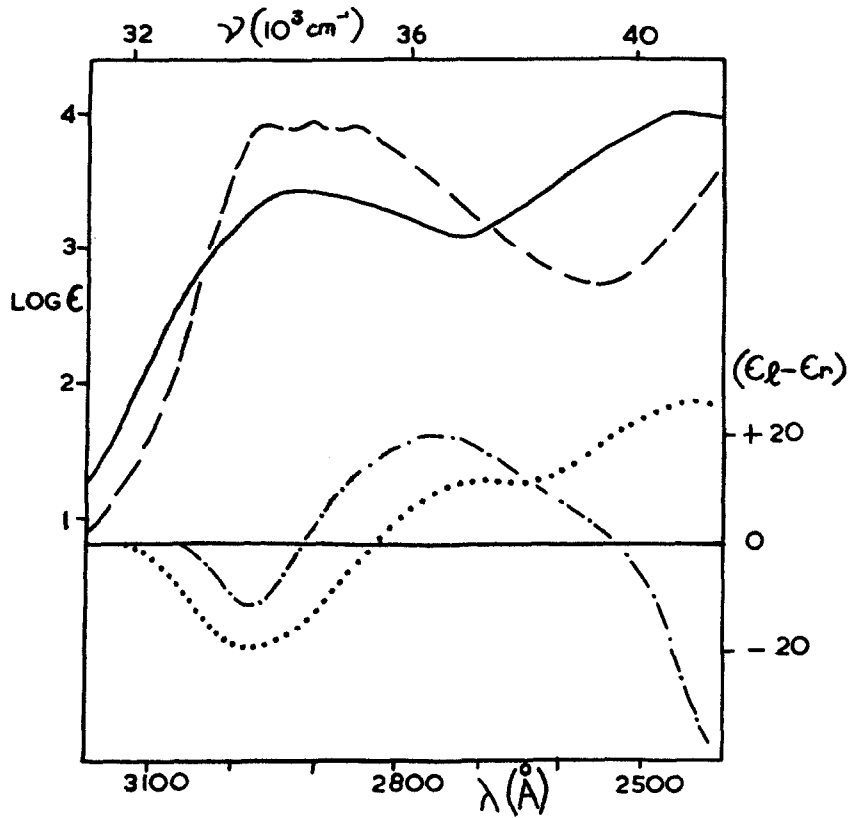
base but the higher energy in argemonine.

From the analysis it is concluded that although the (+)-isomer of Tröger's base and (-)-argemonine give similar Cotton effects in the quartz ultraviolet region they have the opposite configurations (1R,3R) (I) and (1S,5S) (II), respectively. The negative circular dichroism band near 3000Å and the positive band near 2700Å (Fig. 1) originate, respectively, from the A and the B coupling modes of the aniline transition moments in (+)-Tröger's base, whereas in (-)-argemonine they arise, respectively, from the B and the A coupling modes of the transition dipoles of the two veratrole chromophores.

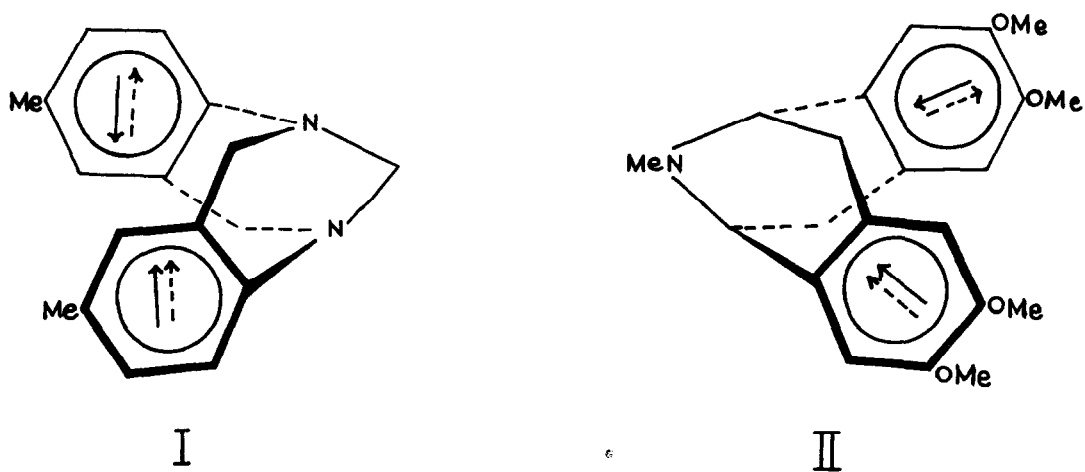
The authors are indebted to Professor V. Prelog (2) for samples of the (+)- and (-)-isomers of Tröger's base and to Professor T. O. Soine (3) for a specimen of (-)-argemonine.

REFERENCES

- (1) O. Cervinka, A. Fabryova and V. Novak, Tetrahedron Letters, 44, 5375 (1966).
- (2) V. Prelog and P. Wieland, Helv. Chim. Acta, 27, 1127.
- (3) M. J. Martell, T. O. Soine and L. B. Kier, J. Amer. Chem. Soc., 85, 1022, (1963).
- (4) F. R. Stermitz, S. Y. Lwo and G. Kallos, J. Amer. Chem. Soc., 85, 1551, (1963)
- (5) S. F. Mason and G. W. Vane, J. Chem. Soc.,(B), 370, (1966).
- (6) J. R. Platt, J. Chem. Phys., 19, 263 (1951).



The absorption spectrum (————) and the circular dichroism (.....) of (+)-Tröger's base, and the absorption spectrum (— — — —) and the circular dichroism (· — · — · — · —) of (-)-argemonine in ethanol, isopentane, ether (2:5:5) at 80°K. For (-)-argemonine the dichroism ordinate is scaled x4.



The A coupling mode (full arrows) and the B coupling mode (dashed arrows) of the low-frequency transition dipoles of the two aniline chromophores in (+)-Tröger's base (I) and of the two veratrole chromophores in (-)-argemonine (II).