The Absolute Configuration of Allenes

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VAN'T HOFF predicted in 1875 that unsymmetrically substituted allenes should exist in two enantiomeric forms.[1] This prediction was not realised experimentally until sixty years later when

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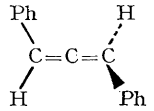
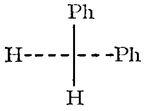
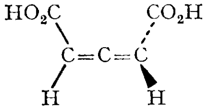
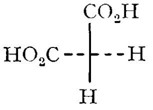
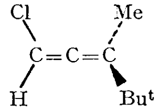
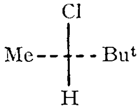
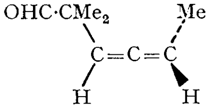
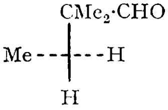
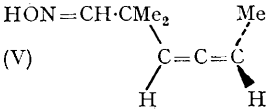
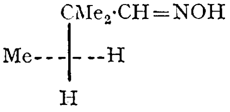
[1] J. H. van't Hoff, "La Chimie dans l'Espace," P. M. Bazendijk, Rotterdam, 1875, p. 29.

Maitland and Mills synthesised the enantiomeric 1,3-diphenyl-1,3-di-α-naphthylallenes by dehydration of 1,3-diphenyl-1,3-di-α-naphthyl-prop-2-en-1-ol with (+)- and (−)-camphor-10-sulphonic acid.[2]

During the last six years the absolute configurations of no fewer than eight allenes have been reported.[3–8] The absolute configurations were, with one notable exception, determined by either the conversion of an optically active molecule of known absolute configuration into an allene or by converting a dissymmetric allene into a molecule of known absolute configuration, by stereochemically unambiguous reactions. In the case of 1,3-diphenylallene (I), an ingenious and fundamental method employing electronic absorption and circular dichroism spectra was used.[3]

	Absolute Configuration of the Allene	*View along the Orthogonal axes*	*Screw pattern of Polarizability*	*Sign of* $[\alpha]_D$	*Configurational Type*[10]
(I)			clockwise	+ve	*S*
(II)			anticlockwise	−ve	*R*
(III)			anticlockwise	−ve	*S*
(IV)			anticlockwise	−ve	*R*
(V)			anticlockwise	−ve	*R*

Five of the allenes (I—V), whose absolute configuration have been established,[3–6] bear substituents which present no problem of conformational asymmetry.[9] These were selected therefore with a view to predicting their sign of rotation.

According to Brewster,[9] a centre of optical activity can usefully be described as an asymmetric screw pattern of polarizability. The high degree of success in predicting the absolute configuration of molecules containing asymmetric carbon atoms using the relative polarizabilities of the substituents suggested that the same principle might apply to dissymmetric allenes. The relative polarizabilities of the substituents found in the allenes (I—V) are as follows, $\mathrm{Cl > Ph > CO_2H > Me > Bu^t > H}$. The relative polarizability of the t-butyl group was deduced by Eliel,[4] the remainder are taken from

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[2] P. Maitland and W. H. Mills, *J. Chem. Soc.*, 1936, 987; *Nature*, 1935, **135**, 994.

[3] S. F. Mason and G. W. Vane, *Tetrahedron Letters*, 1965, 1593.

[4] S. R. Landor and R. Taylor-Smith, *Proc. Chem. Soc.*, 1959, 154; R. J. D. Evans and S. R. Landor, *J. Chem. Soc.*, 1965, 2553 and earlier references there cited; E. L. Eliel, *Tetrahedron Letters*, 1960, No. 8, 16.

[5] W. Agosta, *J. Amer. Chem. Soc.*, 1964, **86**, 2638; 1962, **84**, 110.

[6] E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180.

[7] I. Tömösközi and H. J. Bestmann, *Tetrahedron Letters*, 1964, 1293.

[8] M. H. Gianni, *Diss. Abs.*, 1961, **21**, 2474.

[9] J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475.

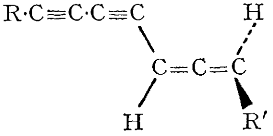
[10] R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 1956, **12**, 81.

Brewster.[9] For the allenes (IV and V) it has been necessary to assume that the polarizability of both $\cdot CMe_2\cdot CHO$ and $\cdot CMe_2\cdot CH{=}N\cdot OH > H$.

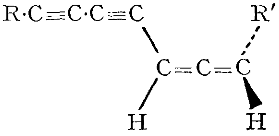
If the allenes are viewed along their orthogonal axes, then the handedness of the screw pattern of polarizability is determined as follows. If by placing the more polarizable substituent in the vertical axis uppermost, the more polarizable substituent in the horizontal axis is to the right, then a clockwise screw pattern of polarizability will obtain and the enantiomer should be dextrorotatory; if the more polarizable substituent in the horizontal axis is to the left, then an anticlockwise screw pattern of polarizability will obtain and the enantiomer should be laevorotatory. It will be seen from the Table that this simple rule predicts correctly the observed sign of the specific rotation. It follows therefore that the sign of rotation together with the above rule can be used to predict the absolute configuration of allenes.

At the present time all the naturally occurring allenes are fungal metabolites, with the exception of fucoxanthin,[11] and laballenic acid.[12] All the dissymmetric fungal allenes contain the rigid diyne-allene system ($R\cdot C{\equiv}C\cdot C{\equiv}C\cdot CH{=}C{=}CH\cdot R'$) where $R{=}H$ or Me.[13] For those metabolites where the group R′ does not introduce conformational asymmetry, the above rule predicts that dextrorotatory enantiomers have the *S*-configuration (VI) and laevorotatory enantiomers have the *R*-configuration (VII).

Although the absolute configuration of a spiran or alkylidenecycloalkane has not yet been reported, it seems likely that a modification of the above rule in which the plane of a ring represents an orthogonal axis, should predict correctly the absolute configuration of such molecules from the sign of their rotation.



(VI)



(VII)

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[11] R. Bonnett, A. A. Spark, J. L. Lee, and B. C. L. Weedon, *Proc. Chem. Soc.*, 1964, 419.

[12] M. O. Bagby, C. R. Smith, and I. W. Wolff, *Chem. and Ind.*, 1964, 1861.

[13] R. E. Bew, J. R. Chapman, Sir Ewart R. H. Jones, B. E. Lowe, and G. Lowe, *J. Chem. Soc.*, 1965, in the press.