Conformations of *trans*, *trans*-Cyclodeca-1,6-diene Derivatives

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Summary ^{1}H n.m.r. spectroscopic data are presented for the preferred conformations of 2,7-dibromo-*trans*- and 2,7-dibromo-*cis*-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-dienes (**1** and **2**, respectively) in deuteriochloroform solution.

In the past few years, there has been much interest[1,2] in the study of the preferred conformations of some medium-ring cycloalkanes and cycloalkenes. We now report some conclusions, based on ^{1}H n.m.r. spectral data, relating to the preferred conformations of two derivatives of *trans,-trans*-cyclodeca-1,6-diene.

Treatment of the bis-dibromocarbene adduct of *cis,cis*-cyclo-octa-1,5-diene with silver perchlorate in methanol solution gave two diastereoisomeric 2,7-dibromo-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-dienes which were isolated in yields of 41 and 6% (see preceding communication[3]). Inspection of the ^{1}H n.m.r. spectrum (Figure a) of the less abundant, higher-melting diastereoisomer reveals that both olefinic protons, τ 3·88 (dd, J 3 and 10·5 Hz), both methine protons, τ 6·33 (dd, J 3·5 and 10 Hz), and both methoxy-groups, τ 6·80 (s), are in identical magnetic environments. It would therefore seem likely that the higher-melting diastereoisomer is the *trans*-dimethoxy-compound, which can take up four principal conformations (**1a**—**1d**) with centres of symmetry. The simplicity of the above ^{1}H n.m.r. spectrum (Figure a) and the sharpness of its signals suggest that one conformer of the higher-melting diastereoisomer is favoured over the others. Furthermore, as one of the coupling constants between the methine protons (3-H and 8-H) and the adjacent methylene protons is relatively large (10 Hz), it seems probable[4] that the methine protons are axially disposed in this favoured conformer. While two of the principal conformers (**1a** and **1b**) have axial methine protons, only in (**1a**) are the relative configurations of the chiral carbon centres (C-3 and C-8) and the chiral *trans*-olefin systems as indicated[5,6] by the ^{1}H n.m.r. spectral data (Figure a).

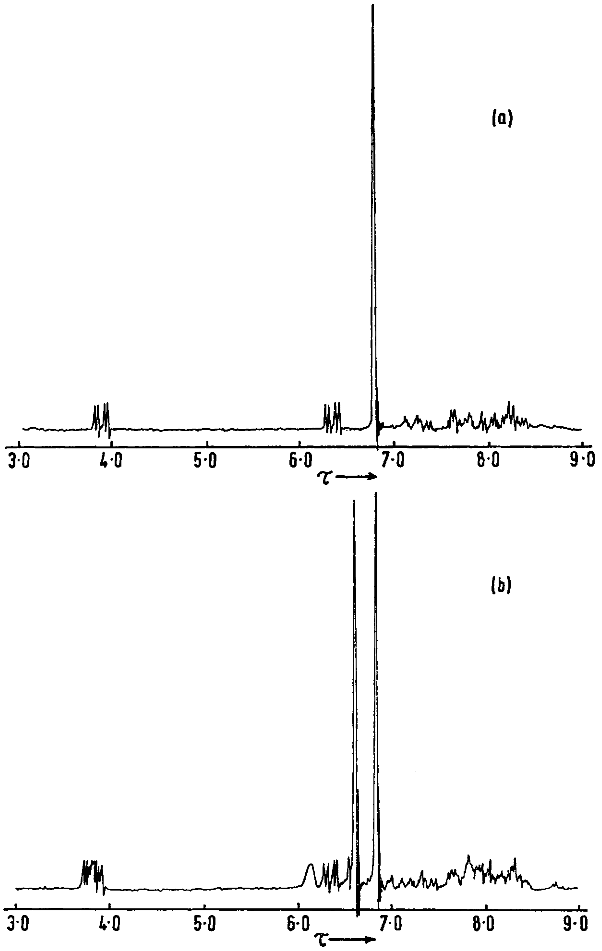
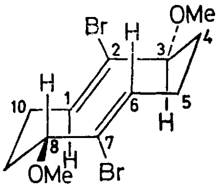
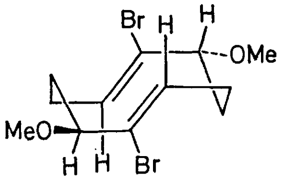


Figure. 100 *MHz* ^{1}H *n.m.r. spectra* (CDCl$_3$ *solution*) *of* (a) *the higher-melting diastereoisomer and* (b) *the lower-melting diastereoisomer of* 2,7-*dibromo*-3,8-*dimethoxy*-trans,trans-*cyclodeca*-1,6-*diene.*

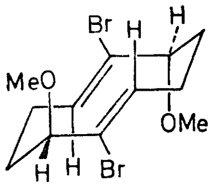
The ^{1}H n.m.r. spectrum of the lower-melting diastereoisomer (Figure b) displays separate signals for the resonance of its two olefinic, τ 3·81 (dd, J *ca.* 2·5 and 10·5 Hz, 1H), 3·87 (dd, J *ca.* 3 and 10·5 Hz, 1H), two methine, τ 6·12 (m, $W_{\frac{1}{2}}$ *ca.* 9 Hz, 1H), 6·35 (dd, J *ca.* 3·5 and 10 Hz, 1H), and two sets of methoxy-protons, τ 6·60 (s, 3H), 6·82 (s, 3H). A noteworthy feature of this spectrum is that the chemical shifts and multiplicities of the higher field olefinic, methine, and methoxy-proton resonances are virtually identical to those of the corresponding signals in the spectrum of the higher-melting diastereoisomer (Figure a and above). Thus, if as seems likely the latter is the *trans*-dimethoxy-compound and has (**1a**) as its preferred conformation, it is reasonable to conclude that the lower-melting diastereoisomer is the *cis*-dimethoxy-compound and that (**2a**) is its preferred conformation. In support of this conclusion, the comparatively narrow signal at τ 6·12 in the ^{1}H n.m.r. spectrum (Figure b) of the lower-melting diastereoisomer suggests the presence of an equatorial methine proton.



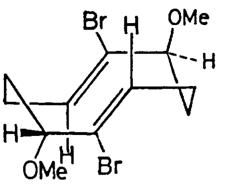
(1a)



(1b)

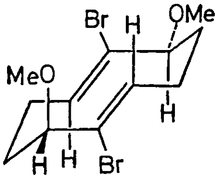


(1c)

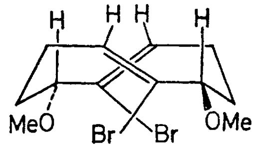


(1d)

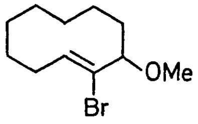
Some uncertainty remains about these conclusions as the *cis*-dimethoxy-compound can also take up conformations such as (**2b**) with non-parallel double bonds. Conformation (**2b**) has a simple two-fold axis of symmetry and if it were its preferred conformation, the *cis*-compound would be expected to have the less complex ^{1}H n.m.r. spectrum (Figure a) observed for the higher-melting diastereoisomer. However, this reversal of stereochemical assignments is unlikely on mechanistic grounds† and, furthermore, an inspection of molecular models suggests that the dipole–dipole and other non-bonded interactions are less in conformation (**2a**) than in (**2b**). Unfortunately, attempts to convert the lower-melting diastereoisomer into the corresponding 1,6-dimethoxycyclodecane, and thereby establish the relative configurations of its methoxy-groups with certainty, were unsuccessful.



(2a)



(2b)



(3)

The diastereoisomeric 2,7-dibromo-3,8-dimethoxy-*trans*,-*trans*-cyclodeca-1,6-dienes (**1** and **2**) both appear to have much more conformational stability than 2-bromo-3-methoxy-*trans*-cyclodecene (**3**).[6] Thus, the methoxy-signals in the ^{1}H n.m.r. spectrum of the lower-melting diastereoisomer coalesce at 158° (hexachlorobutadiene solution). At 190°, the low field region of the ^{1}H n.m.r. spectrum of the latter compound [in C_4Cl_6 solution: τ 3·92 (t, J 7 Hz), 6·37 (m), 6·85 (s)] corresponds closely to that of (**3**)[6] at 35°.

The conclusions relating to the conformational preferences of the 2,7-dibromo-3,8-dimethoxy-*trans*,*trans*-cyclodeca-1,6-dienes (**1** and **2**) cannot be assumed to hold for the parent hydrocarbon. It is possible that steric and electrostatic factors due to the presence of the 2- and 7-bromo-substituents in (**1**) and (**2**) are critical in determining the conformational preferences of these compounds.

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† The bis-dibromocarbene adduct of *cis*,*cis*-cyclo-octa-1,5-diene has been reported[7] to consist of 5 parts of the *syn*- and 1 part of the *anti*-isomer. As Ag$^+$-assisted methanolysis of the mono-dibromocarbene adduct of *cis*,*cis*-cyclo-octa-1,5-diene appears[5] to take place on the same side as the leaving group, the major methanolysis product of the mixture of bis-dibromocarbene adducts would be expected to be the *cis*-dimethoxy-compound (**2**), derived from the more abundant *syn*-adduct.

[1] J. Dale, *Pure Appl. Chem.*, 1971, **25**, 469.
[2] J. D. Dunitz, *Pure Appl. Chem.*, 1971, **25**, 495.
[3] C. B. Reese and A. Shaw, preceding communication.
[4] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, 1957, **79**, 1005.
[5] C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1365.
[6] C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1367.
[7] E. K. Dehmlow and G. C. Ezimora, *Tetrahedron Letters*, 1970, 4047.