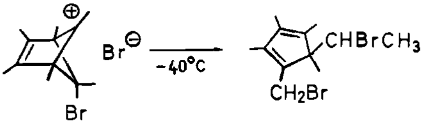
Methylenchlorid allerdings gut lösliche Bromverbindung **9**. Ein Analogon zur thermischen Umlagerung von **9** in das Cyclopentadienderivat **10** konnten wir für die Chlorverbindung nicht beobachten.



9 **10**

In SO_2 ist **8** bis $-10°$, der höchsten von uns gemessenen Temperatur, stabil. In Methylenchloridsuspension zersetzt sich **8** bei $-20°$ unter Eliminierung von Chlorwasserstoff.

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134. Crystal Structure Analysis of a *trans*, *trans*-Cyclodeca-1,6-diene Derivative

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(29. III. 73)

Summary. An X-ray crystal structure analysis of the higher melting diastereoisomer of 2,7-dibromo-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (monoclinic; $a = 5.76$, $b = 10.43$, $c = 11.32$ Å, $\beta = 94.04°$; space group $P2_1/n$; $Z = 2$) has confirmed the NMR. assignment of the molecular conformation and the *trans* configuration of the methoxy groups. The *trans,trans*-

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cyclodeca-1,6-diene ring adopts a centrosymmetric crown conformation with a C—C=C—C torsion angle of 162°.

Reese & Shaw [1] have deduced from NMR. spectra that the higher melting diastereoisomer of 2,7-dibromo-3,8-dimethoxy-*trans, trans*-cyclodeca-1,6-dene occurs almost exclusively in the centrosymmetric crown conformation (Fig. 1). An X-ray crystal structure analysis was undertaken in order to confirm this assignment and to provide structural information about the hitherto neglected cyclodecadienes.

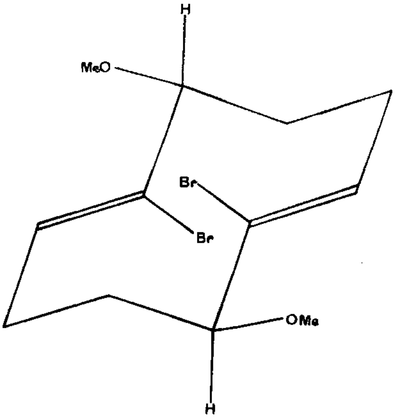

Fig. 1. *Conformation of 2,7-dibromo-3,8-*trans-*dimethoxy*-trans, trans-*cyclodeca-1,6-diene*

The X-ray results concur with *Reese & Shaw*'s conclusion; the 10-membered ring in this molecule occurs in a crown-like conformation, in preference to the alternative conformation with C_2 symmetry (Fig. 2). The C–C=C–C torsion angle is 162°, significantly different from the usual value of 180° for an unstrained *trans*-substituted double bond. This kind of deformation is a consistent feature of medium rings containing *trans* double bonds and is thought to involve out-of-plane bending of the bonds about the trigonal atoms as well as twisting around the double bond [2] [3]. Both kinds of distortion have been found to occur in non-planar amide bonds, as in caprylolactam [4]. In the compound described here, one of the trigonal atoms is fully substituted so that the extent of out-of-plane bending at this atom can be assessed.

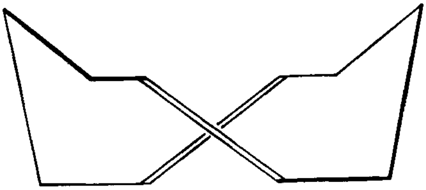

Fig. 2. *Alternative conformation of* trans, trans-*cyclodeca-1,6-diene system*

Experimental. – 2,7-dibromo-*trans*-3,8-dimethoxy-*trans, trans*-cyclodeca-1,6-diene, $C_{12}H_{18}O_2Br_2$; M. W. 354.09; monoclinic, $a = 5.76$, $b = 10.43$, $c = 11.32$ Å, $\beta = 94.04°$; $D_m = 1.70$, $D_x = 1.73$ g cm^{-3}, $Z = 2$; space group $P2_1/n$; linear absorption coefficient (MoKα radiation); $\mu = 63.2$ cm^{-1}.

Crystals suitable for X-ray analysis were kindly supplied by *C. B. Reese & A. Shaw* of Cambridge University. Cell constants were measured by diffractometry (MoKα radiation, λ = 0.7107 Å). The intensities of 701 independent reflexions ($\theta < 26°$) were measured on the *Hilger & Watts* Y290 computer-controlled four-circle diffractometer ($\theta/2\theta$ scan, scan width 0.8° in 0.01° steps, one second per step, background count of 20 sec 0.5° (θ) on each side of peak maximum, standard reflexion measured after every 30 intensity measurements). The crystal decomposed during data collection; the intensity of the standard reflexion fell by 30% of its initial value. The intensities were accordingly rescaled on the basis of a linear regression through the intensities of the standard reflexion. The crystal used was a small needle of dimensions 0.1 × 0.1 × 0.3 mm. No corrections were made for absorption.

Table 1. *2,7-dibromo-*trans*-3,8-dimethoxy-*trans, trans*-cyclodeca-1,6-diene; fractional atomic coordinates and mean isotropic vibration parameters* $\langle U \rangle = 1/3\,(U_{11} + U_{22} + U_{33})$. Estimated standard deviations × 10^4 in parameters. Atom numbering as in Fig. 3.

	x	y	z	⟨U⟩
Br	0.2042(6)	0.2109(3)	−0.1293(2)	0.0653(16)
C(1)	−0.0450(42)	0.1583(21)	−0.0457(18)	0.0466(133)
C(2)	−0.1912(47)	0.0657(22)	−0.0819(20)	0.0541(149)
C(3)	−0.1841(50)	−0.0164(24)	−0.1904(21)	0.0691(168)
C(4)	−0.1811(45)	−0.1642(20)	−0.1599(19)	0.0586(146)
C(5)	0.0372(40)	−0.2037(21)	−0.0855(17)	0.0456(117)
C(6)	0.2559(54)	−0.3918(27)	−0.0382(25)	0.0804(197)
O	0.0323(30)	−0.3423(14)	−0.0893(14)	0.0569(103)

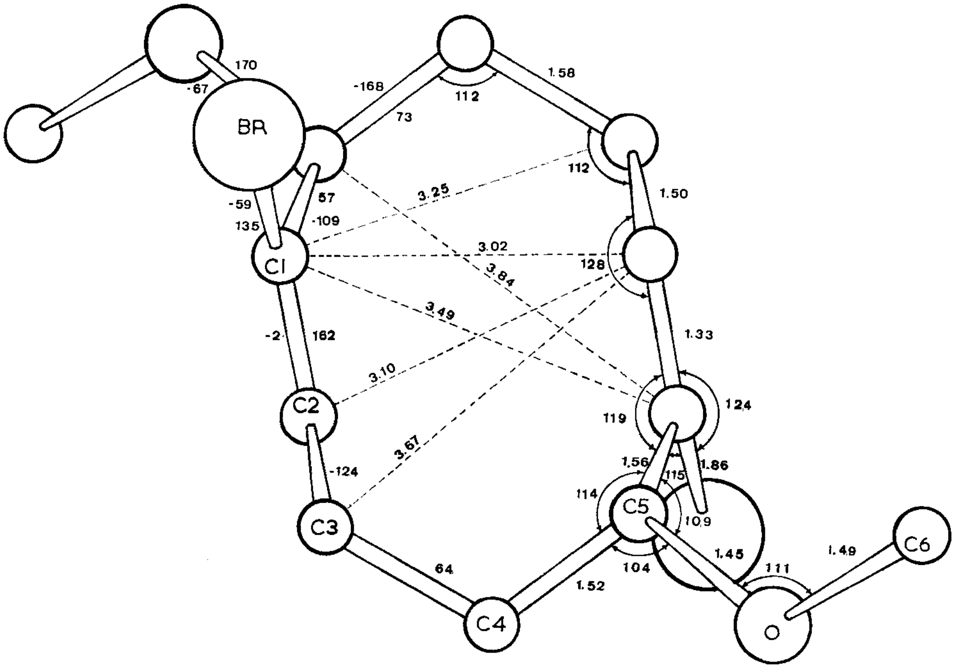

Fig. 3. *View of molecule projected on the plane through the four atoms of the diene system.* Interatomic distances (mean.e.s.d. 0.03 Å) are in Å, bond angles (mean.e.s.d. 2°) and torsion angles (mean. e.s.d. 3°) in degrees.

The structure was solved by a straightforward application of the heavy atom method. All of the light atoms (excluding hydrogens) were located in the first F_0-*Fourier* synthesis phased on Br contributions, and six cycles of full-matrix least-squares calculations reduced the value of $Q = \Sigma\omega_i\,(F_o - F_c)^2$ from 44275 (Br anisotropic; C, O isotropic vibration parameters) to 8666 (Br, O, C anisotropic; H atoms included in structure factor calculations only, using calculated positions and estimated isotropic vibration parameters), at which point refinement was judged to be essentially complete (R = 9.7%). Unit weights ($\omega_i = 1$) were used throughout.

Discussion. – A detailed discussion of the molecular geometry would be inappropriate, considering the limited accuracy of this structure determination. The molecular dimensions, calculated from the final atomic positions (Table 1), are shown in Fig. 3.

The out-of-plane bending at C(1) amounts to 16°, C(1) being displaced by 0.12 Å (σ = 0.03 Å) from the plane through Br, C(2) and C(5'). The displacement is outward,

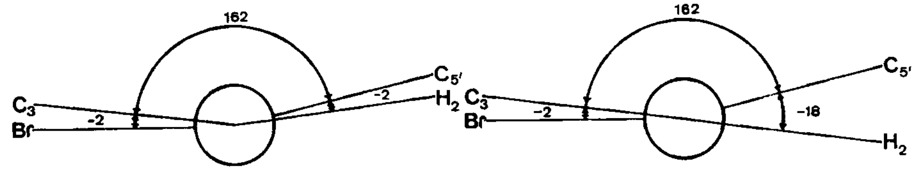

Fig. 4. *Two possible torsion angle relationships around the double bond.* The actual situation probably lies somewhere between these extremes.

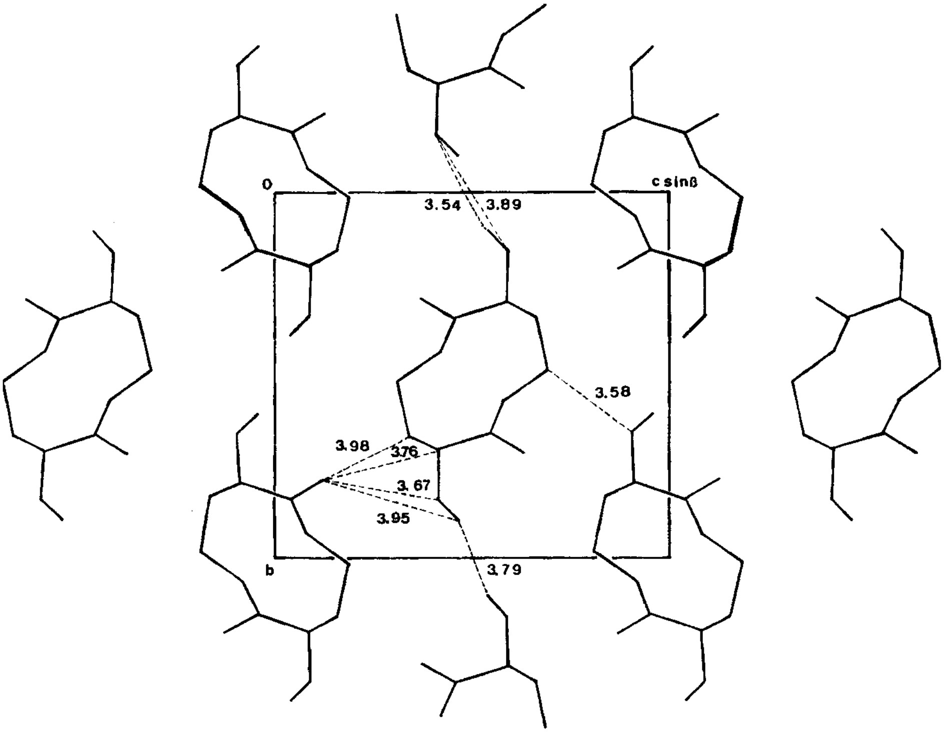

Fig. 5. *Packing diagram with intermolecular distances in Å*

i.e. away from C(2′). The magnitude and direction of out-of-plane bending at C(2) is unknown but it is likely to be in the same sense, *i.e.* outward, and it is unlikely to be greater than at C(1). The angle relationships round the double bond are thus probably between the two extreme situations depicted in Fig. 4, and the twist angle τ [4] should lie between 2° and 10°. The molecular packing arrangement is shown in Fig. 5 with intermolecular contacts less than 4 Å.

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135. Thermische Reaktionen mit 3-Phenyl-2*H*-azirinen; 1,3-dipolare Cycloadditionen und En-Reaktionen

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(23. III. 73)

Summary. Benzonitrile *p*-nitrobenzylide (**5**) undergoes 1,3-dipolar cyclo-additions in the presence of 3-phenyl-2*H*-azirines (**1**), yielding in benzene at 0° 2-(*p*-nitrophenyl)-4,5-diphenyl-1,3-diazabicyclo[3.1.0]hex-3-enes (**7**, scheme 2). Under the basic conditions of the reaction mixture, **7a** and **7b** are partially converted to 2-(*p*-nitrophenyl)-4,5-diphenyl-1,6-dihydropyrimidines (**8a, b**) which are dehydrogenated by oxygen to the corresponding pyrimidines **9a** and **9b**, respectively.

3-Phenyl-2*H*-azirines (**1**) form, on heating at 145° in xylene in the presence of the azlactone **32** (2,4-diphenyl-Δ^2-oxazolin-5-one), 4-(aziridin-2′-yl)-2,4-diphenyl-Δ^2-oxazolin-5-ones (**33**, scheme 11). **33** arises from an ene reaction of the enol form of **32** with **1**. Similar ene reactions are observed with the azirines **1** and dimedone (**37**, scheme 12). Under the ene reaction conditions (xylene, 145°), the non-isolated intermediate primary adducts (**38a** and **38b**) undergo rearrangements of the vinylcyclopropane-cyclopentene type to give 6,6-dimethyl-4-oxo-1,3-diphenyl-4,5,6,7-tetrahydroisoindole (**40**) and 6,6-dimethyl-4-oxo-3-phenyl-4,5,6,7-tetrahydroindole (**42**), respectively.

1. Einleitung. – Das photochemische Verhalten von 3-Phenyl-2*H*-azirinen (**1**) ist in den letzten Jahren sehr intensiv untersucht worden (vgl. dazu [1]). Die beim Bestrahlen mit Quecksilber-Hochdrucklampen hinter Pyrex sich bildenden Benzonitril-methylide **2** können durch 1,3-dipolare Cycloadditionen an Carbonylgruppen [2], aktivierte Doppelbindungen [3], Dreifachbindungen [2a, b] und kumulierte Doppelbindungen [4] abgefangen werden (Schema 1).

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