265. The Structures of Medium-Ring Compounds. Part XVII.
Crystal and Molecular Structures of *cis*-cyclodecene · $\frac{1}{2}$ $AgNO_3$ and 1,1,4,4-Tetramethyl-*cis*-cyclodec-7-ene · $\frac{1}{2}$ $AgNO_3$

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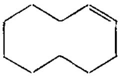
Summary. The crystal structures of *cis*-cyclodecene. $\frac{1}{2}$ $AgNO_3$ (monoclinic, $a = 5.329$, $b = 14.53$, $c = 27.17$ Å, $\beta = 92.02°$, space group $C\ 2/c$) and of 1,1,4,4-tetramethyl-*cis*-cyclodec-7-ene · $\frac{1}{2}$ $AgNO_3$ (orthorhombic, $a = 5.879$, $b = 16.86$, $c = 28.39$ Å, space group $C222_1$) have been determined. The relative arrangement of Ag^+ cations, NO_3^- anions and cyclo-olefin molecules are very similar in the two crystals, but the conformations of the ring skeletons are very different.

cis-Cyclodecene (I-*cis*) has the smallest heat of hydrogenation (20.7 kcal mole^{-1}) of all known olefins [1] and must therefore adopt a conformation of particularly low strain energy, even after allowing for the rather large strain energy of the hydrogenated product, cyclodecane. The heat of hydrogenation of *trans*-cyclodecane (I-*trans*) is about 3.3 kcal mole^{-1} larger than that of the *cis*-isomer [1]. Of the six 1,1,4,4-tetramethylcyclodecenes [II–IV, *cis* and *trans*] prepared by *Sicher et al.* [2] the isomer III-*cis* occurs to more than 90% in the equilibrium mixture and has a heat of hydrogenation of 22.0 kcal mole^{-1}, close to that of I-*cis*, suggesting that its conformation is similar to that of the unsubstituted olefin. The least stable of the six isomers is IV-*cis* with a heat of hydrogenation of 28.7 kcal mole^{-1}, 2.7 kcal mole^{-1} *larger* than that of IV-*trans*, showing that it cannot adopt the energetically favourable conformation of I-*cis*. These results can be nicely accomodated within the framework of a structural model based on the stable cyclodecane conformation, assuming it to be preserved as far as possible in the unsaturated compounds [2] [3].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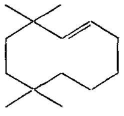
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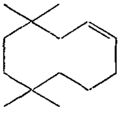
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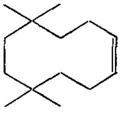
IV

In order to obtain experimental evidence on the conformations of these olefins we have determined the structures of their crystalline $AgNO_3$ adducts. The results obtained for *trans*-cyclodecene · $\frac{1}{2}$ $AgNO_3$ have already been described [4]. We report here the results of crystal structure analyses of the *cis*-cyclodecene · $\frac{1}{2}$ $AgNO_3$ and 1,1,4,4-tetramethyl-*cis*-cyclodec-7-ene · $\frac{1}{2}$ $AgNO_3$ adducts.

1. *Preparation of Crystals.*

An equimolar amount of olefin was poured on the surface of an aqueous $AgNO_3$ solution and covered with a layer of methanol. The white, microcrystalline precipitate obtained was recrystallized from cold methanol (– 30°C) to give needles elongated along [100]. For the *X*-ray study the crystals were enclosed in *Lindemann* glass capillaries since they otherwise lose olefin on standing in the open at room temperature. The crystals turn black on exposure to *X*-radiation with gradual loss in the quality of the diffraction pattern.

2. *Crystallographic data.*

(*cis*-Cyclodecene)$_2$ AgNO$_3$ (subsequently abbreviated to CCA), $(C_{10}H_{18})_2$ AgNO$_3$, M.W. 446.4, monoclinic, $a = 5.329$, $b = 14.53$, $c = 27.17$ Å, $\beta = 92.02°$, $U = 2102$ Å^3, $D_m = 1.40$, $D_x = 1.41$, $Z = 4$, space group $C\,2/c$ (C^6_{2h}) or $C\,c$ (C^4_s) – the former was assumed and confirmed by the subsequent structure analysis.

(1,1,4,4-Tetramethyl-*cis*-cyclodec-7-ene)$_2$ AgNO$_3$ (TMCCA), $(C_{14}H_{26})_2$ AgNO$_3$, M.W. 558.6, orthorhombic, $a = 5.879$, $b = 16.86$, $c = 28.39$ Å, $U = 2815$ Å^3, $D_m = 1.3$, $D_x = 1.318$, $Z = 4$, space group $C222_1$ (D^5_2).

The reported cell dimensions are based on measurements on 30°-precession photographs made with Cu$K\alpha$ radiation ($\lambda = 1.542$ Å) and are accurate to within about 1 part in 500.

3. *Intensity Measurements.*

For both crystals, the diffraction pattern was recorded with Mo$K\alpha$ radiation on the *Hilger & Watts* linear diffractometer equipped with scintillation counter (Sr/Zr balanced filters, oscillation angle 2°–5° depending on width of diffraction maxima in different layers, counter-collimator 1 mm diameter, measurement time approximately 140 s per reflexion).

The CCA crystal had linear dimensions approximately $0.1 \times 0.2 \times 0.3$ mm and was mounted to give the layers hKl ($K = 0$ to 11). A total of 1477 independent reflexions were examined.

The TMCCA crystal had linear dimensions approximately $0.2 \times 0.3 \times 0.4$ mm and was mounted to give the layers Hkl ($H = 0$ to 6). A total of 1405 independent reflexions were examined.

The observed intensities were converted to relative F^2-values in the usual way without any special correction for absorption (linear absorption coefficients for Mo$K\alpha$ radiation are 9.6 cm^{-1} for CCA and 7.3 cm^{-1} for TMCCA).

4. *Structure Analysis.* CCA, TMCCA and the analogous complex with *trans*-cyclodecene [4] crystallize in different space groups, but the similarities in cell dimensions suggest that the three crystal structures are closely related. The observed regularities in the distributions of the strong reflexions show, in particular, that the relative arrangements of the heavy Ag$^+$ ions are virtually the same in all three cases.

For CCA the distribution of strong reflexions placed the Ag$^+$ ions at the special positions $4e(2): 0, y, \frac{1}{4}$, etc. with y approximately 0.20 (assuming $C\,2/c$ as space group). The positions of the other non-hydrogen atoms could be recognized without difficulty in the *Fourier* synthesis based on the signs of the Ag$^+$ contributions to the structure factors. The nitrate groups, as expected, are also located on the dyad axes of the space group.

The space group $C222_1$ of TMCCA requires the Ag$^+$ and NO$_3^-$ ions to occupy special positions on dyad axes $4b(2): 0, y, \frac{1}{4}$, etc. or $4a(2): x, 0, 0$, etc. The intensity distribution shows that the first of these possibilities, with y approximately 0.08, is the correct one for the Ag$^+$ ions. A *Fourier* synthesis, calculated with the phases of the Ag$^+$ contributions, led again to the location of all remaining non-hydrogen atoms.

5. *Structure refinement.* The structure parameters for both crystals were refined by full-matrix least-squares analysis. The models incorporated anisotropic vibrational parameters for the Ag$^+$ ions, and individual isotropic vibrational parameters for the carbon, nitrogen, and oxygen atoms.

For the later stages of refinement, the positions of hydrogen atoms were estimated by stereochemical considerations and the contributions of these atoms were included in the calculated F-values. An isotropic vibrational parameter, set equal to that of the attached carbon atom, was assigned to each hydrogen atom.

For CCA six refinement cycles led to a conventional R factor of 0.065, based on the 709 reflexions included in the final refinement cycle. For TMCCA the R factor after seven refinement cycles was 0.061, based on 889 significant reflexions.

A fuller account of the structure refinement including details of the weighting systems and tables of observed F-values with estimated standard deviations is given elsewhere [5].

6. Results. The results of the crystal structure analyses are presented in Tables 1 and 2 for CCA, and in Tables 3 and 4 for TMCCA, and are illustrated in Fig. 1 and 2.

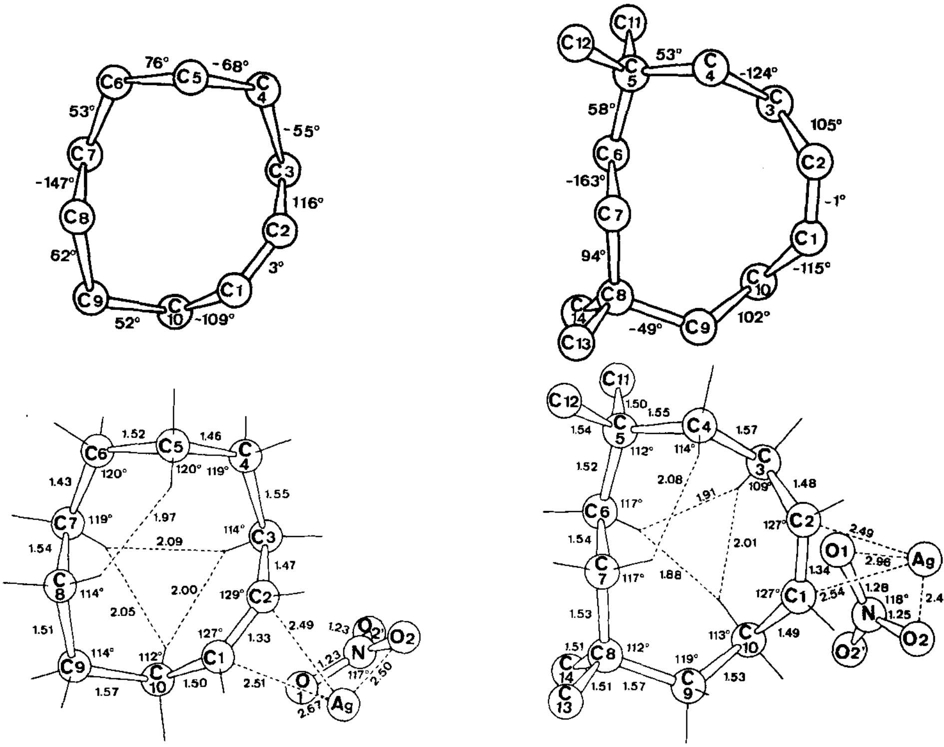

Fig. 1. *Interatomic distances, bond angles and torsion angles found in CCA* (left) *and TMCCA* (right)
The atom-numbering corresponds to that in Tables 1, 2, 3, 4

The standard deviations listed in Tables 1 and 3 were calculated by inversion of the least-squares normal equations matrix. The anisotropic vibrational parameters of the Ag atoms (Tables 1 and 3) correspond to the expression

$$\exp.\ [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

5. Discussion. The conformations found for the ring skeletons of *cis*-cyclodecene and of 1,1,4,4-tetramethylcyclodec-7-ene in their crystalline $AgNO_3$ adducts are quite different, as indicated by the different torsion angle patterns shown in Fig. 1. The conformation of the unsubstituted cyclo-olefin resembles the stable conformation of cyclodecane, whereas that of the tetrasubstituted cyclo-olefin is quite different. A more detailed discussion of the observed conformations with respect to the chemical

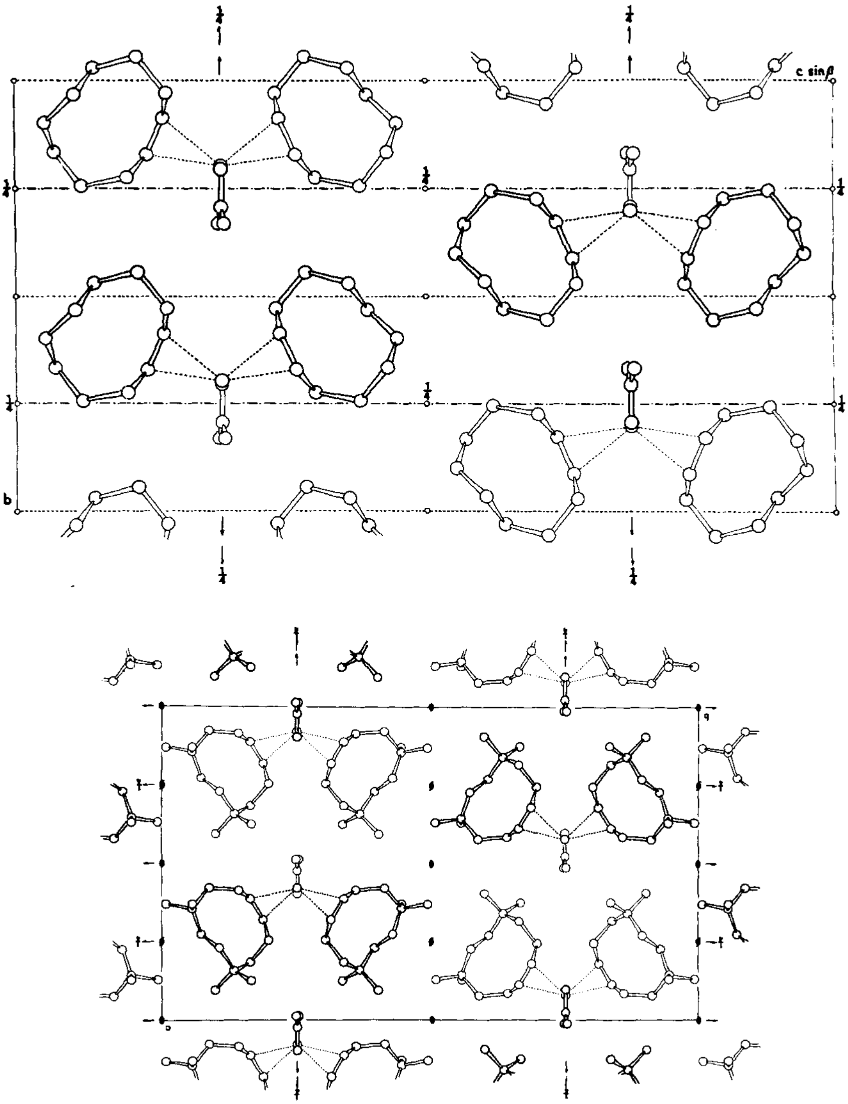

Fig. 2. *Crystal structures of CCA and TMCCA shown in projection along the [100] direction*

and thermochemical properties of cyclo-olefins will be given in a separate communication [6].

The crystal structures of CCA and TMCCA are illustrated in Fig. 2; they are obviously very similar to one another and also to the previously described $AgNO_3$ complex of *trans*-cyclodecene [4]. All three structures are characterized by the presence of $Ag^+ \ldots NO_3^- \ldots Ag^+$ chains in the [100] direction; these chains are, in turn, associated into ionic layers perpendicular to the [001] direction. The ionic layers are separated by the hydrocarbon molecules which can be regarded as being loosely

Table 1. *CCA: Positional and vibrational parameters from least-squares analysis*
Standard deviations in brackets (units of least significant digit)

	x	y	z		B (Å^2)
C(1)	– 0.0092 (29)	0.0866 (13)	0.1793 (5)		5.18 (35)
C(2)	– 0.0306 (27)	0.1700 (11)	0.1598 (5)		4.79 (34)
C(3)	0.1613 (29)	0.2250 (11)	0.1358 (6)		5.47 (37)
C(4)	0.1010 (34)	0.2444 (14)	0.0804 (7)		6.94 (44)
C(5)	0.0498 (33)	0.1666 (13)	0.0474 (6)		6.63 (43)
C(6)	0.2591 (36)	0.1004 (15)	0.0358 (7)		7.68 (49)
C(7)	0.3414 (38)	0.0336 (15)	0.0717 (7)		7.98 (50)
C(8)	0.1464 (31)	– 0.0296 (13)	0.0946 (6)		6.33 (40)
C(9)	0.2108 (38)	– 0.0558 (15)	0.1475 (8)		8.11 (51)
C(10)	0.2238 (31)	0.0286 (13)	0.1838 (6)		6.21 (40)
O(1)	1/2	0.2082 (15)	1/4		6.03 (33)
O(2)	0.2945 (22)	0.3318 (8)	0.2463 (4)		6.84 (29)
N	1/2	0.2931 (17)	1/4		4.70 (35)
Ag	0	0.19792 (17)	1/4		
b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0.04749 (83)	0.00903 (15)	0.00142 (3)	0	0.00460 (20)	0

Table 2. *CCA: Estimated positional parameters of H-atoms*
(assumed: local C_{2v} symmetry about each C atom; C—H distance, 1.1 Å; HCH angle for methylene groups, 106°)

	x	y	z
H(1)	– 0.1810	0.0566	0.1939
H(2)	– 0.2168	0.2022	0.1617
H(3A)	0.1851	0.2908	0.1554
H(3B)	0.3433	0.1895	0.1396
H(4A)	– 0.0622	0.2908	0.0780
H(4B)	0.2590	0.2834	0.0659
H(5A)	– 0.1033	0.1263	0.0628
H(5B)	– 0.0253	0.1946	0.0122
H(6A)	0.2013	0.0629	0.0021
H(6B)	0.4236	0.1416	0.0263
H(7A)	0.4825	– 0.0104	0.0547
H(7B)	0.4411	0.0705	0.1019
H(8A)	– 0.0381	0.0044	0.0928
H(8B)	0.1257	– 0.0925	0.0723
H(9A)	0.0711	– 0.1053	0.1602
H(9B)	0.3920	– 0.0921	0.1492
H(10A)	0.2509	0.0041	0.2219
H(10B)	0.3894	0.0710	0.1763

associated into double layers. In the 1:1 $AgNO_3$ complexes of germacratriene [7] and of cyclodeca-*cis,trans*-1,5-diene [8] the ionic $AgNO_3$ layers are quite analogous to those occurring here, but they are separated only by single layers of hydrocarbon molecules.

Table 3. *TMCCA: Positional and vibrational parameters from least-squares analysis*
Standard deviations in parentheses (units of least significant digit)

	x	y	z	B (Å^2)
C(1)	0.0448 (24)	0.1123 (7)	0.1635 (4)	3.17 (23)
C(2)	0.0091 (46)	0.1804 (6)	0.1869 (4)	3.43 (21)
C(3)	0.1769 (24)	0.2440 (8)	0.1966 (4)	3.41 (25)
C(4)	0.1309 (29)	0.3161 (8)	0.1630 (5)	4.04 (28)
C(5)	0.3395 (28)	0.3406 (8)	0.1332 (5)	3.62 (26)
C(6)	0.4383 (21)	0.2704 (7)	0.1065 (4)	3.14 (24)
C(7)	0.2776 (27)	0.2268 (8)	0.0723 (5)	3.86 (27)
C(8)	0.3494 (30)	0.1443 (10)	0.0560 (5)	3.11 (31)
C(9)	0.2430 (25)	0.0776 (9)	0.0878 (4)	3.87 (25)
C(10)	0.2605 (24)	0.0848 (8)	0.1414 (4)	3.45 (23)
C(11)	0.5172 (46)	0.3747 (8)	0.1650 (5)	4.91 (29)
C(12)	0.2587 (31)	0.4051 (9)	0.0987 (5)	5.13 (34)
C(13)	0.2555 (27)	0.1306 (9)	0.0072 (5)	4.13 (29)
C(14)	0.6024 (34)	0.1304 (12)	0.0553 (7)	4.86 (46)
O(1)	1/2	0.0982 (7)	1/4	5.60 (28)
O(2)	0.3132 (15)	–0.0128 (5)	0.2532 (6)	4.90 (19)
N	1/2	0.0225 (7)	1/4	3.43 (24)
Ag	0	0.07833 (8)	1/4	

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0.03968 (58)	0.00392 (6)	0.00110 (2)	0	0.00253 (36)	0

In CCA and in TMCCA the Ag^+ ions are coordinated to the double bonds in an approximately symmetrical fashion (Ag...C, 2.49 and 2.51 Å in CCA, 2.49 and 2.54 Å in TMCCA; for comparison, 2.42 and 2.46 Å in the *trans*-cyclodecene complex [4]). These distances are all somewhat longer than those found in complexes where each Ag^+ is coordinated to one double bond, for example, 2.40 Å in cyclonona-*cis,cis,cis*-1,4,7-triene · $3AgNO_3$ [9], 2.38 Å in humulene · $2AgNO_3$ [10] and 2.36 Å in norbornadiene · $2AgNO_3$ [11]. On the other hand, there is no marked dependence of the Ag...C distances on the configuration of the double bond.

The shortest Ag...O distances are 2.50 Å in CCA and 2.40 Å in TMCCA (for comparison 2.49 Å in the *trans*-cyclodecene complex [4]). The mean N–O distances in the planar NO_3^- anions are 1.23 Å in CCA, 1.26 Å in TMCCA and 1.23 Å in the *trans*-cyclodecene complex; little significance can be attached to these differences in view of the rather large standard deviations.

In TMCCA the presence of the methyl groups must contribute substantially to the tighter packing of the molecules in the hydrocarbon double-layers (as evinced by the strikingly smaller temperature factors than in CCA). The shortest intermolecular C...C distance in TMCCA is 3.74 Å (between the methyl carbon C(11, x, y, z) and C(4, $x + 1$, y, z)), whereas the shortest corresponding C...C distances in CCA are 3.97 Å.

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Table 4. *TMCCA: Estimated positional parameters of H-atoms*
(assumed: local C_{2v} symmetry about each C atom; C—H distance, 1.1 Å; HCH angle for methylene groups, 106°; methyl groups staggered)

	x	y	z
H(1)	– 0.1020	0.0723	0.1604
H(2)	– 0.1643	0.1902	0.2002
H(3A)	0.3511	0.2216	0.1917
H(3B)	0.1659	0.2628	0.2337
H(4A)	0.0740	0.3672	0.1840
H(4B)	– 0.0112	0.3015	0.1393
H(6A)	0.5029	0.2272	0.1323
H(6B)	0.5876	0.2910	0.0866
H(7A)	0.2540	0.2642	0.0409
H(7B)	0.1092	0.2221	0.0889
H(9A)	0.3208	0.0208	0.0775
H(9B)	0.0616	0.0727	0.0787
H(10A)	0.3987	0.1261	0.1504
H(10B)	0.3092	0.0272	0.1564
H(11A)	0.4457	0.4255	0.1844
H(11B)	0.6657	0.3921	0.1439
H(11C)	0.5749	0.3286	0.1897
H(12A)	0.1873	0.4559	0.1181
H(12B)	0.4073	0.4226	0.0776
H(12C)	0.1280	0.3801	0.0753
H(13A)	0.3072	0.0711	– 0.0046
H(13B)	0.3300	0.1772	– 0.0151
H(13C)	0.0707	0.1407	0.0077
H(14A)	0.6541	0.0709	0.0436
H(14B)	0.6768	0.1771	0.0330
H(14C)	0.6707	0.1404	0.0908

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