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CONFORMATION OF CYCLOOLEFINS.
CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPLEX $AgNO_3$-(TRANS-CYCLODODECENE)$_2$

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The structural investigation of the complex $AgNO_3$(trans-cyclododecene)$_2$ has been undertaken as part of a research on the structure of cycloolefins performed in our laboratory in the last few years.

Crystals of $AgNO_3$(trans-$C_{12}H_{22}$)$_2$ were prepared by reacting an aqueous solution of $AgNO_3$ with a solution of $C_{12}H_{22}$ in ether. Pure trans-cyclododecene was obtained by means of chromatographic separation of a commercial mixture of cis and trans isomers.

X-ray diffraction studies of single crystals of the complex showed it to be orthorombic; space group Pbcn with unit cell dimensions $a = 5.46 \pm 0.01$A°, $b = 14.50 \pm 0.03$Å, $c = 30.57 \pm 0.06$Å; $D_o = 1.35$ g·cm^{-3}($D_c = 1.36$ g·cm^{-3}), Z = 4. The silver atom and NO_3 group are in the special positions ½, y, 1/4; 0, y, 1/4 respectively. Intensities of 933 non-zero independent reflections were obtained with normal Weissenberg techniques using CuK_α radiation. The intensities were corrected for absorption effects.

A three-dimensional Patterson map yielded the position of the Ag atom. Fourier synthesis showed the location of the light atoms. The refinement

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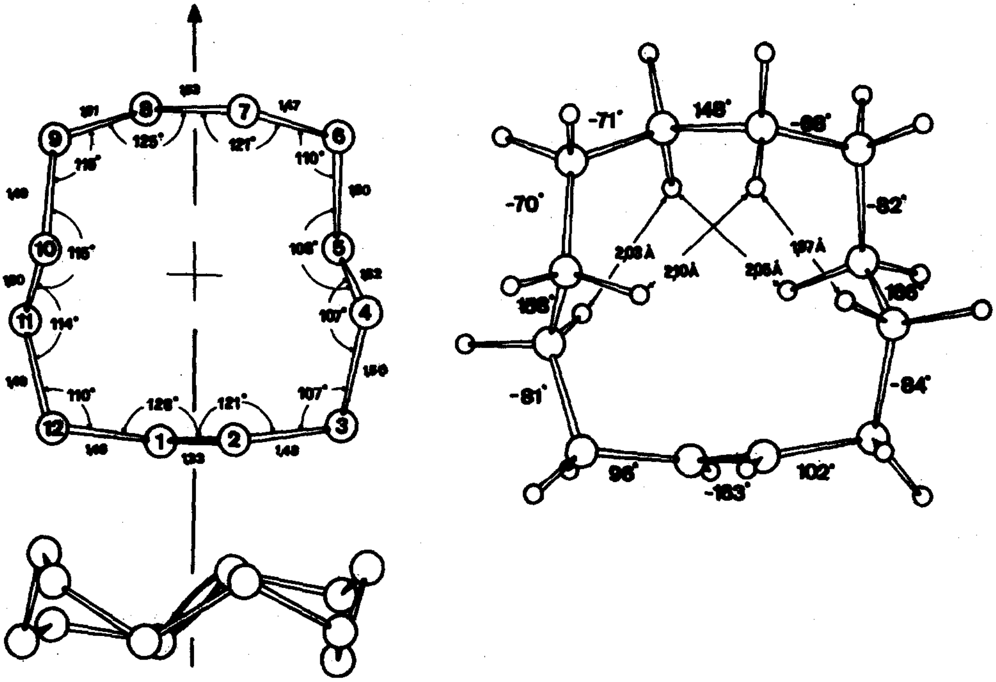
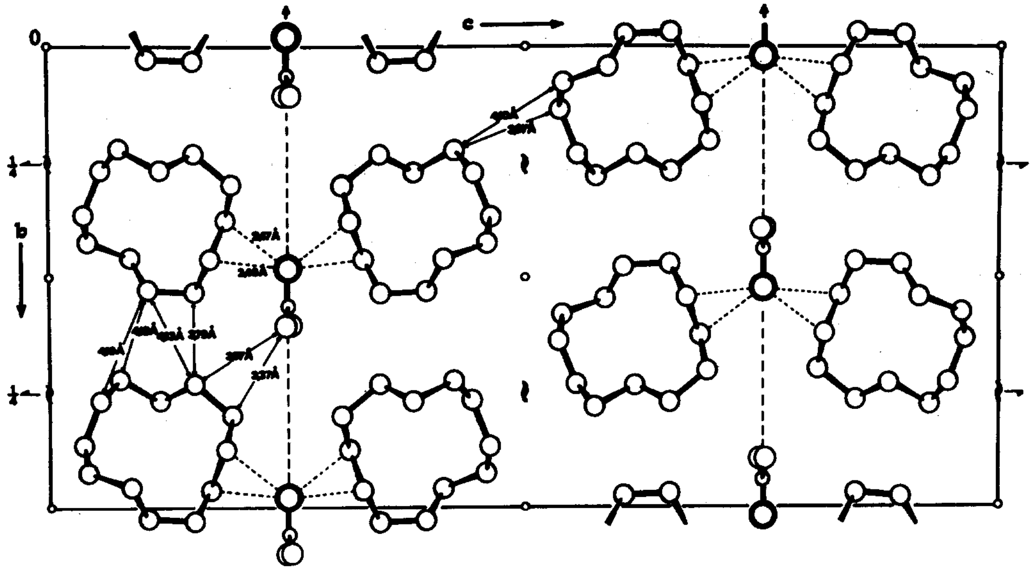
** Istituto Chimico dell'Università di Napoli, V. Mezzocannone 4, 80134 Napoli, Italy of the structure was performed with least squares program to give an R value of 0.09. The standard deviations for the bond lengths are ca. 0.01Å; for the bond angles ca. 0.5°.



I Conformational parameters of the trans-cyclododecene ring

The conformation of trans-cyclododecene is characterized by a pseudo C_2 symmetry (Fig. I). The molecular parameters of the saturated part of the ring are rather similar to those found for cyclododecane(1) and for 13,13 dimethyl-13-azoniabicyclo [10.1.0] tridecane iodide.(2) The group $\mathrm{C}\diagup^{\mathrm{C}}\diagdown\mathrm{C}\diagup^{\mathrm{C}}$ shows a deviation from planarity of 17°. The corresponding deviation in trans-cyclooctene is 45°(3) and in trans-cyclodecene is 40°.(4) As expected, the non planar distortion of the grouping $\mathrm{C}\diagup^{\mathrm{C}}\diagdown\mathrm{C}\diagup^{\mathrm{C}}$ decreases with increasing size of the cycloolefinic ring; however it is still high. Unlike the cases of trans-cyclooctene and trans-cyclodecene no intra-anular non-bonded interactions can be invoked to explain this distortion (see Fig. 1). Probably the electronic interactions between Ag and the double bond play, in this case, the most important role. This result suggests that also in the previously reported structures(3,4) the contribution to the non planar distortion of the $C^{\nearrow C\searrow}C^{\nearrow C}$ grouping due to the electronic interactions with the coordinated metal atom may be higher than supposed.



II Projection of the structure of $AgNO_3$(trans-cyclododecene)$_2$ on [100].

Fig. II shows the projection of the structure of $AgNO_3$(trans-cyclododecene)$_2$ on [100]. The mode of packing is very similar to that found in the case of the corresponding complex with trans-cyclodecene.

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