2,8,10,11-tetrachloro-12-oxahexacyclo-
[7.2.1.02'8.03'7.04'11.06'10]dodeca-1,9-diol and
disorder and mixed crystals in a system of tetracyclo-
[6.3.0.04'11.05'9]undecanone and undecanol derivatives

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Received November 15, 1993

2,8,10,11-Tetrachloro-12-oxahexacyclo[7.2.1.02'8.03'7.04'11.06'10]dodeca-1,9-diol is a strained
cage molecule containing six five-membered rings and a four-membered ring. Twenty-five of the
internal angles are less than 105° with 6 ranging from 89.5(3) to 97.4(3)°. The base promoted
reaction of 3,6-dipyridyl-1,2,4,5-tetrazine with tetracyclo[6.3.0.04'11.05'9]undecane-3,6-dione
yields the monoketone 6,7-[3',6'-di(2''-pyridyl)-4',5'-pyridazino]tetracyclo[6.3.0.04'11.05'9]
undecan-2-one. This compound crystallizes in the centrosymmetric space group P21/n with en-
tantiomers related by a center of symmetry. In the crystal investigated the molecules are disordered
with each site containing about 80% of one isomer and 20% of the enantiomer. When the ketone
is hydrogenated and the product isolated, two different crystals were found to have a ratio of
alcohol to ketone of 0.71/0.29 and 0.75/0.25 or about 3/1. The alcohol and ketone occupy the same
sites, but with opposite stereochemistries.

Introduction

Cage compounds of the type 1 to 5 are of interest
because of their large strain energies, high densities and
facile rearrangements. We have been interested in the
bonding in these systems and the energetics of rear-
rangement (Watson et al., 1992, 1994; Aleksandrov et
al., 1993). Compound 6 is a readily accessible deriva-
tive of 2, and the details of the structure are reported.

As part of a program concerned with the synthesis
and chemistry of novel polycyclic “cage” compounds
(Marchand, 1989, 1991), the synthesis of several new
“molecular clefts” have been reported (Marchand et al.,
1988, 1990). When tetracyclo[6.3.0.04'11.05'9]unde-
cane-3,6-dione (1a) is reacted with one equivalent of
3,6-dipyridyl-1,2,4,5-tetrazine the enantiomeric mon-
oketones 7a and 7b can be isolated (Scheme 1). Reac-
tion with a second mole of the tetrazine produces a mo-
lecular cleft which may be modified further. An X-ray
investigation of compound 7 showed the crystal to be
disordered but not randomly. The compound crystal-
lizes in a centrosymmetric space group with enantio-
mers related by a center of symmetry. In the crystal investigated the molecules are disordered
with each site containing about 80% of one isomer and 20% of the enantiomer. When the ketone
is hydrogenated and the product isolated, two different crystals were found to have a ratio of
alcohol to ketone of 0.71/0.29 and 0.75/0.25 or about 3/1. The alcohol and ketone occupy the same
sites, but with opposite stereochemistries.

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Experimental

Compound 6 was prepared by the Diels-Alder reaction of chloranil with cyclopentadiene followed by UV photolysis and reaction of the photoproduct with a weak base. Compound 7 (Haddadin et al., 1994) was recrystallized from CH₂Cl₂—MeOH to yield pale yellow crystals melting at 233.5–234.0°C. Compound 7 was reduced with NaBH₄ to yield endo alcohol 8. Compound 8 was recrystallized from CH₂Cl₂—MeOH to give very pale yellow crystals. All data were collected on a Rigaku AFC-6S diffractometer using the ω-2θ mode at a fixed scan rate with multiple scans for weak reflections. The data were collected with Cu Kα radiation (λ = 1.54178 Å). Lorentz-polarization corrections, a Ψ-scan empirical absorption correction and an isotropic extinction correction were applied. The structures were solved by direct methods (Sheldrick, 1986) and were refined by a full-matrix least-squares technique with a weighting scheme based on the measured esd's. Computer programs used were TEXSAN (Molecular Structure Corporation TEXSAN, 1985), SHELXS86 (Sheldrick, 1986), and PLATON-92 (Spek, 1990). The crystal and refinement data are given in Table 1. Atomic positional parameters for compounds 6, 7, and 8 are given in Tables 2, 3, and 4 while selected bond lengths and bond angles are given in Tables 5 and 6 for compound 6 and Tables 7 and 8 for compounds 7 and 8. Figures 1, 2, and 3 are thermal ellipsoid drawings of molecules 6, 7, and 8.

Discussion

Compound 6 is composed of a planar four-membered ring (σₚₚ = 0.003 Å) and six five-membered rings fused into a closed cage structure. The five-membered rings are all in the envelope conformation with ϕ(2) for each ring differing from nx36° by no more than 3° (Boeyens, 1978). Molecular mechanics investigations of 1 indicate the strain energy is associated with valence angle distortion (132 kJ/mol) and torsional interactions (158 kJ/mol) with a smaller repulsion term associated with van der Waals and dipolar repulsion (Watson et al., 1994; Allinger et al., 1989; PMODEL, 1988). This is consistent with the 25 internal valence angles of less than 105° and the bond eclipsing created by the symmetric cage structure. Dipolar repulsion is responsible for the elongation of the C(1)—C(7) and C(9)—C(10) bonds to 1.59 Å or greater in 1 and its derivatives, and this elongation is not modeled well by molecular mechanics with most existent parameter sets (Watson et al., 1994). Compound 6 shows larger valence angle strain (150 kJ/mol) and torsional strain (178 kJ/mol) contributions than in 1, but a reduction associated with van der Waals and dipole repulsion terms. The