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# [8](3,7)TROPOLONOPHANE

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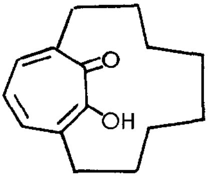
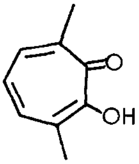
Abstract  The first single-decked tropolonophane has been synthesized  The compound exists in the near-planar enolone form with no flipping of the bridge  However, a keto form was isolated on its azo coupling

The distortion of aromatic rings and the resulted modification in their aromatic properties are a major part of interest in the studies of phanes  In the previous paper[1)], we described synthesis, some physical properties and chemical behaviors of [2]paracyclo[2](3,7)tropolonophane  In order to evaluate directly the effect of distortion of tropolone ring, we have synthesized [8](3,7)tropolonophane 1, the first single-decked tropolonophane, and investigated some of its physical properties and chemical behaviors in comparison with its open chain analog, 3,7-dimethyltropolone 2[2)]

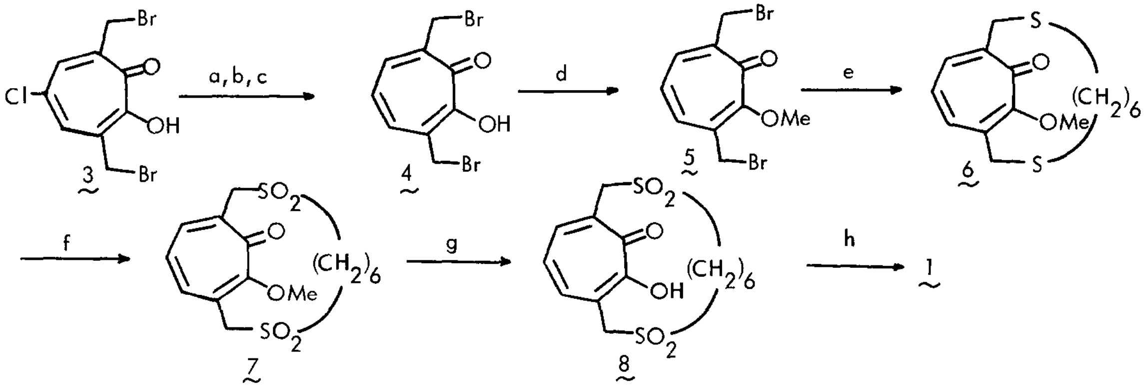


1



2

Synthesis  The desired tropolonophane 1 was synthesized in 8 steps by the route shown below starting from the known tropolone 3[1,3)]



a MeOH, ref , 87% yield  b $H_2$/Pd-C, KOH-$H_2O$, 93%  c HBr, 100°C, 85%  d $CH_2N_2$, 87%  e $HS(CH_2)_6SH$, $NaOCH_3$-MeOH, high dilution, 45%  f $H_2O_2$, 0°C, 76%  g HBr-HOAc, 100°C, 96%  h 530-540°C, 2 Torr , 18%

As the catalytic hydrodechlorination of strained chlorotropolone in previous phane system proceeded in poor yield1), chlorine was reduced this time at an earlier stage 3 → 4 As alternate to the route 7 → 8 → 1, 7 can be first thermolyzed (480-500°C, 2 Torr ) to the methylether 9 of 1 in 5 2% yield, acid hydrolysis of which in turn gave 1 in 74% yield Compound 1 was obtained as colorless needles, m p 32-34 5°C, after purification via its Cu salt, m p > 300°C

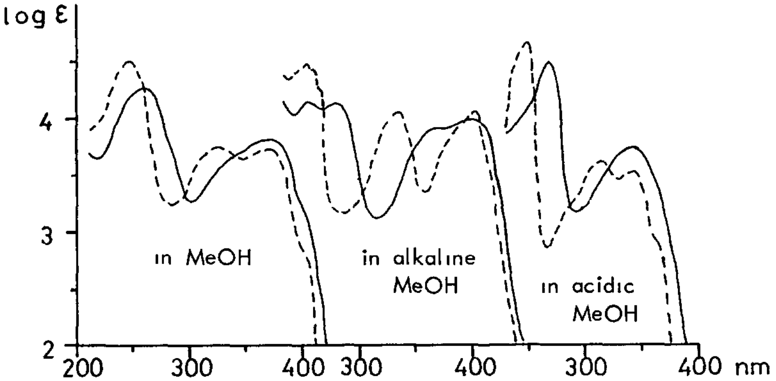


Fig 1 Electronic Spectra of 1 (——) and 2 (---)

Diketone-Enolone Problem IR spectrum of 1, exhibiting a broad OH band at ca 3100 cm$^{-1}$ and strong band at ca 1550 cm$^{-1}$ but no band at normal carbonyl region, is very similar to that of 2 Electronic spectrum of 1 (Fig 1) is also similar to that of 2 through some bathochromic shift with a loss of fine structure, both general features in short bridged phanes4), is noted The similar features are observed also in alkaline and acidic media (Fig 1) These spectra suggest the enolone structure for 1

Its NMR spectra (PMR spectrum, Fig 2) are compatible only with enolone but not with diketone structure Signals due to tropolone moiety appear at 7 24 (2H, d, J=10 0, H$_4$), 6 86 ppm (1H, t, J= 10.0, H$_5$), and 169 8 (C$_1$), 139 8 (C$_3$), 136 9 (C$_4$), 126 2 ppm (C$_5$), which are all comparable with those of 2 (7 36 (2H, d, J=10), 6 86 (1H, t, J=10), 168 2, 134 6, 138 3, 125 4 ppm, respectively) Bridge carbons appear as 4 sharp singlets (35 1 (α), 29 4 (β), 25 7 (γ), 27 7 ppm (δ))5) in proton-noise decoupled CMR spectrum The number of these signals verifies the rapid tautomerism on the NMR time scale occurring at room temperature

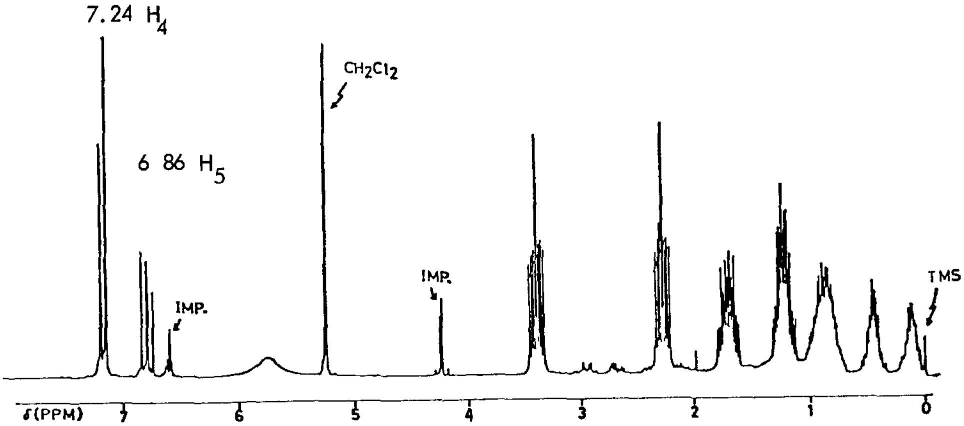
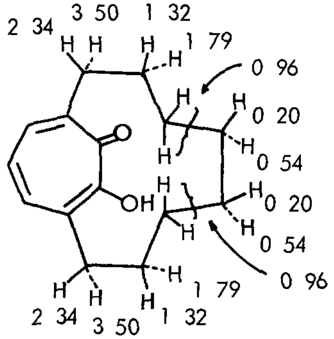


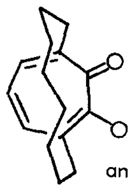
Fig 2 PMR Spectrum of 1 (CD$_2$Cl$_2$+ CF$_2$Cl$_2$)

*Planarity of Tropolone Ring* Although the crystals of 1 are not suited for X-ray crystallographic analysis, CMR chemical shifts provide information about planarity of the tropolone ring Chemical shift differences observed between 1 and 2 [$C_3$ (+5 2 ppm, + denotes down field shift), $C_4$ (-1 4 ppm) and $C_1$ (+1 6 ppm)] are explicable by an alkyl substituent effect[6] Thus CMR spectrum suggests 1 has a planar tropolone ring while electronic spectra (*vide supra*) may suggest slight deformation of the ring

*Conformation of Bridge* High field signals in PMR spectrum of 1 can be assigned as shown to bridge hydrogens in analogy with [8]paracyclophane[5]

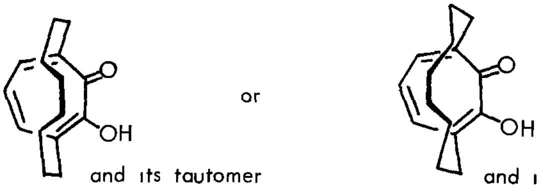


Although the bridge does not flip from one side of tropolone ring to the other, as is suggested by the nonequivalence of α-hydrogens, it is not rigid and undergoes conformational change at room temperature This was witnessed by the change of the all signals upon cooling, though complete analysis was not possible At -100°, tropolone hydrogens appear as two sets of signals composing of an ABC ($\delta_A$ 6 85, $\delta_B$ 7 11, $\delta_C$ 7 26 ppm, $J_{AB}$=10 0, $J_{AC}$=9 2, $J_{BC}$=0 8) and $AB_2$ ($\delta_A$ 6 71, $\delta_B$ 7 19, $J_{AB}$=10 0) (intensity ratio *ca* 3 1) Since the $AB_2$ pattern can be resulted only from the tautomerizing tropolone system, the process slowed down is the conformational change in the bridge, and the two conformers must be as shown below The free energy difference between them was calculated from the intensity ratio to be *ca* 300 cal/mol



and its tautomer

major conformer

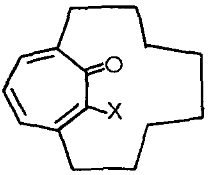


and its tautomer

and its tautomer

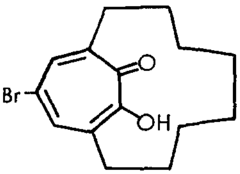
minor conformer

*Chemical Reactions* Compound 1 shows positive $FeCl_3$ color reaction characteristic to tropolones Diazomethane yielded liquid methyl ether 9[7], which can be converted quantitatively to methylaminotropone 10 Compound 1 undergoes electrophilic reactions Bromination (Cu salt) gives the bromotropolone 11 in 37% yield (Cf 77% yield for 2) Phenyldiazonium chloride couples with 1 to give rather unstable dark orange red crystals 12, m p 67-74°C (decomp ) On the basis of IR (no OH, $\nu_{CO}$ 1683, 1663 $cm^{-1}$) and PMR ($AX_2$, A=4 93 ppm, X=6 73 ppm, $J_{AX}$ 7 2 Hz), the diketo structure 12 was

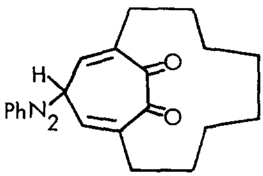


9 X=OMe

10 X=NHMe



11



12

assigned Attempted nitrosation of 1 afforded unidentified yellow powder, m p 156-158°C, whose spectra revealed it not to be simple tropolone derivatives Thus, compound 1 was shown to possess somewhat modified tropolone structure and behave as such

## References and Notes

1) N. Kato, Y Fukazawa and S Itô, Tetrahedron Letters, 1113 (1979)

2) T Nozoe, T Mukai and K Takase, Sci Repts Tohoku Univ , Series I, **36**, 41 (1952)

3) Selected spectral data of the intermediates 4 pale yellow needles, m p 165-166°C, m/e 310, 308, 306 (1 2 1 $M^+$), 119 (b p ), $\delta$ 7 77 (2H, d, J=10 0), 7 10 (1H, t, J=10 0), 4 77 (s, 4H) 5 pale yellow needles, m p 106 5-107°C, m/e 324, 322, 320 (1 2 1 $M^+$), 243 (b p ), 241, $\delta$ 7 50 (1H, dd, J=8 3, 1 5), 7 09 (1H, dd, J=11 4, 1 5), 6 85 (1H, dd, J=11 4, 8 3), 4 58 (2H, s), 4 50 (2H, s), 4 05 (3H, s) 6 pale yellow prisms, m p 64 5-66°C, m/e 310 ($M^+$), 108 (b p ) 7 pale yellow prisms, m p 242°C, m/e 374 ($M^+$), 108 (b p ), $\nu$ 1570, 1118 $cm^{-1}$ 8 pale yellow powder, m p $\geq$ 265°C (decomp ), m/e 360 ($M^+$), 91 (b p ), $\nu$ 3140, 1593, 1548, 1116 $cm^{-1}$

4) N L Allinger, L A Freiberg, R B Hermann and M A Miller, J Am Chem Soc , **85**, 1171 (1963) B H Smith, "Bridged Aromatic Compounds", p 359 Academic Press, New York, N Y (1964) D J Cram, C S Montgomery and G R Knox, J Am Chem Soc , **88**, 575 (1966)

5) Assignment followed well established general trend of chemical shifts in [n]paracyclophanes T Kaneda, T Otsubo, H Hirota and S Misumi, Bull Chem Soc Jpn , **53**, 1015 (1980)

6) Although the effect caused by the change of alkyl groups on CMR chemical shift of tropolone carbon is not known, it is known in benzene derivatives [J B Stothers, "Carbon-13 NMR Spectroscopy", p 97 Academic Press, New York, N Y (1972)] A similar but less pronounced effect is observed in 2,7-disubstituted tropones (Y Mazaki, unpublished result) The chemical shifts of 1 are comparable within ~1 ppm with those of di-n-butyltropolone calculated from the shifts of 2, applying the alkyl substituent effect

7) Spectral data of [8](3,7)tropolonophane derivatives 9 pale yellow oil, m/e 246 ($M^+$, b p ), $\lambda_{max}^{MeOH}$ 251 (log $\epsilon$ 4 17), 318 (3 55), 350 sh (3 51) nm, $\nu$ 1619, 1603 $cm^{-1}$, $\delta^{CDCl_3+CCl_4}$ 0 65-1 92 (12H, m), 2 19 (2H, complex m), 3 20 (2H, complex m), 4 02 (3H, s), 6 63 (1H, dd, J=11 3, 6.4), 6 68 (1H, dd, J=11 3, 2 1), 6 79 (1H, dddd, J=6 4, 2 1, 1 2, 1 0) 10 yellow granules, m p 101-102°C, m/e 245 ($M^+$, b p ), $\lambda_{max}^{MeOH}$ 257 5 (log $\epsilon$ 4 01), 287 (3 82), 376 sh (3 77), 412 (3 82) nm, $\nu$ 3240, 1588, 1559 $cm^{-1}$, $\delta^{CCl_4}$ 0 28-1 85 (12H, m), 2 12 (1H, ddd, J=12 0, 9 0, 4 5), 2 36 (1H, ddd, J=14 1, 8.3, 4 5), 2 99 (1H, m), 3 07 (3H, br s), 3 56 (1H, ddd, J=12 0, 6 0, 4 5), 6 37 (1H, dd, J=10 5, 8 6), 6 88 (1H, br d, J=10 5), 7 04 (1H, br d, J=8 6) 11 colorless needles, m p 68-70°C, m/e 312, 310 (1 1, $M^+$), 185 (b p ), $\lambda_{max}^{MeOH}$ 251 (log $\epsilon$ 4 04), 269 sh (3 98), 286 sh (3.65), 368 (3 71), 380 sh (3 69), 414 sh (3 24) nm, $\nu$ 3220, 1595, 1550 $cm^{-1}$, $\delta^{CCl_4}$ 0 20-0 80 (4H, m), 0 87-1 22 (4H, m), 1 39 (2H, m), 1 73 (2H, m), 2 27 (2H, ddd, J=12 2, 7 6, 4 6), 3 47 (2H, ddd, J=12 2, 7 6, 4 6), 7 37 (2H, s) 12 additional spectral data, m/e 336 ($M^+$), 77 (b p ), $\lambda_{max}^{MeOH}$ 215 sh (log $\epsilon$ 4 09), 220 sh (4 05), 250 sh (4 09), 258 (4 10), 265 (4 10), 281 sh (3 95), 302 sh (3 88), 372 (3 72), 407 (3 72), 440 sh (3 69) nm

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