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1,11-o-BENZENO[2]ORTHOCYCLO[1](6,8)HEPTAFULVENOPHANE
A NEW ROUTE TO HEPTAFULVENE FROM 8,8-DICHLORO-3-ALKYL-4-OXATRICYCLO[5,1,0,0^{3,5}]OCTANE

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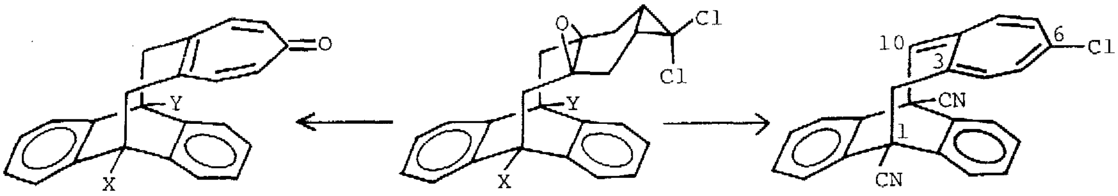
Abstract: The title compound, which has a highly distorted heptafulvene, was obtained unexpectedly from the 8,8-dichloro-3-alkyl-4-oxatricyclo-[5,1,0,0^{3,5}]octane derivative when treated with $TiCl_4$ in benzene solution.

Our interest in expanding the scope of intramolecular charge transfer type interactions between the nonbenzenoid and benzenoid aromatics recently led us to a successful synthesis of 1,11-o-benzeno[2]orthocyclo[2](4,5)-troponophane(**1**).[1)] The method we applied for the synthesis of the tropone ring is acid treatment of a dihalo-epoxide(**2**), as recently developed by Kato.[2)] Although trifluoroacetic acid treatment of both **2a** and **2b** gave the respective desired products(**1a** and **1b**) in moderate yields, when applied to **2c** it gave **1c** in poor yield. In order to find better reaction conditions for **2c**, we tested various acids and found that $TiCl_4$ gave the unanticipated heptafulvene derivative(3) in rather high yield. In this communication we report on the structure and physical properties of this unique product.



1a-c

2a X=Y=H
b X=H,Y=CN
c X=Y=CN

3

When **2c** was treated in dry benzene with $TiCl_4$ at room temperature, yellow prisms were generated in 62% yield, as a single isolable product. The structure of the product was deduced to be 1,11-o-benzeno[2]orthocyclo[1]-(6,8)heptafulvenophane(3) from spectral data.[3)] ^{1}H-NMR resonances of five vinylic protons are characteristic for the heptafulvene skeleton. The vicinal coupling constants ($J_{H4,H5}$ =7.3Hz, $J_{H7,H8}$ =10.7Hz) for the heptafulvene ring protons are much smaller than those of corresponding values of planar 8,8-dicyanoheptafulvene(**4**)[4)] (8.0Hz and 12.0Hz, respectively), suggesting a nonplanar structure for this skeleton. The yellow color of the crystal is also an indication of its nonplanarity, since the heptafulvene itself gives red colored crystals.$^{5)}$ In order to confirm this and to determine the precise geometry for this unique structure, an X-ray crystallographic analysis for **3** was undertaken.

X-ray crystallographic analysis for 3: The crystallographic data for 3 are given in Table 1 and the molecular geometry is illustrated in Figure 1.

Table 1. Crystallographic data for 3.

Crystal system	Monoclinic
M. F.	$C_{25}H_{15}N_2Cl$
M. W.	378.86
Space group	$P2_1/c$
a	8.779(2)Å
b	28.925(8)
c	7.804(1)
β	105.72(1)°
Z	4
Reflections	3079
R	0.068

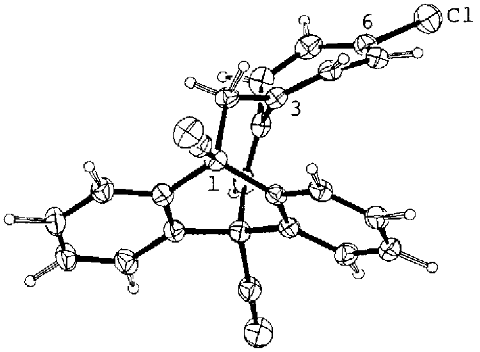
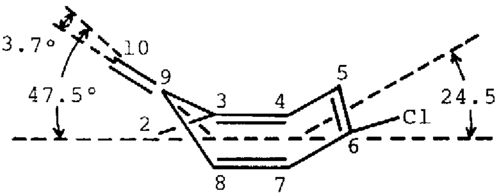
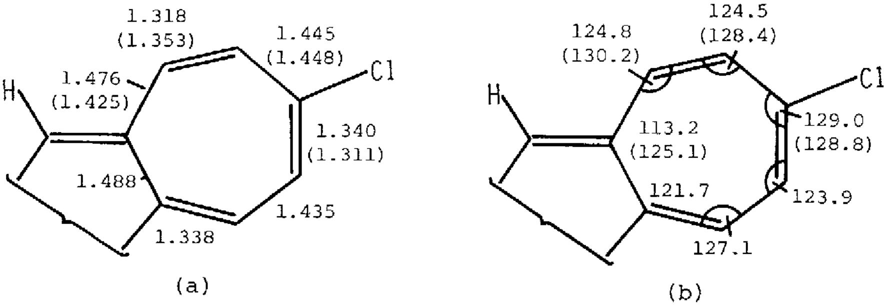


Fig.1. Molecular structure of **3**.

As is clearly shown in this Figure, a nonplanar heptafulvene skeleton is condensed onto the four carbon bridge of the dibenzobicyclo[4.2.2]decatrienylidene system. The heptafulvene ring is deformed to a boat conformation, the bow (C9) is elevated by 47.5° and the stern (C5-C6) by 24.5° with respect to a line connecting points midway between C3-C8 and C4-C7. These deformation angles are quite similar to the corresponding values for the derivative of 7,7-dimethyl-cycloheptatriene-3-carboxylic acid (thujic acid) (52.3° and 23.2°, respectively).$^{6)}$ A small inward bending (3.7°) of the exocyclic double bond (C9=C10) from the bow plane was found. Similar inward bending of the exocyclic double bonds (C=O) were also





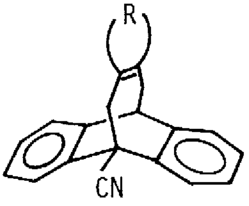
(a) (b)

Fig.2. Bond lengths(a) and angles(b) of the heptafulvene ring of **3** and those of **4**(in parenthesis).

observed in the boat forms of heavily distorted tropone skeletons in [4]-7) and [3](2,7)troponophanes.8)

Other deformations of the heptafulvene ring were also observed with respect to the bond angles and bond lengths in **3**. Almost all the inner ring angles for the heptafulvene group are smaller than those of the planar molecule **4**.9) In particular, the angle at the bow (C9) is 113.2° compared to the value of 125.4° in **4**.

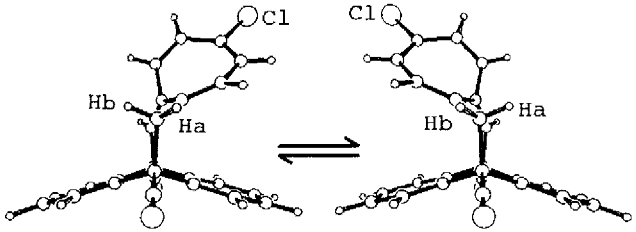
As previously reported, the buteno bridge in **1** has a folded structure that flips rapidly to its mirror image at room temperature. Replacement of one sp^3 carbon of the buteno bridge by an sp^2 carbon induces it to be closer to perpendicular as was found both in **Ia** and **Ib**.10) However the four carbon bridge for 3 still has a folded structure, as is clearly seen in Figure 1. Hence the flipping of the bridge should be operative in solution at room temperature.1)



Ia $R=-(CH_2)_2-$
b $R=-(CH_2)_3-$

Dynamic process: In the ^{1}H-NMR spectra for **3**, the signals due to the methylene protons appear as two unresolved broad peaks at room temperature, suggesting a conformational equilibrium between the two equivalent folded structures, as shown below. In this case flipping of the four carbon bridge causes concomitant inversion of the heptafulvene boat form.

Variable temperature ^{1}H-NMR spectra for 3 were then examined in order to obtain the activation energy for this flipping process. The methylene signals became a well split AB quartet at -20°C. When the temperature was raised, each signal became broad at around 20°C, almost disappear at 50°C, and then reappeared as a broad signal at around 70°C. Above this temperature the signal gradually became sharp and eventually give a sharp singlet at 120°C, as is shown in Figure 3. The free energy of activation was deduced to be 14.8kcal/mol from the coalescence temperature. Apparently,



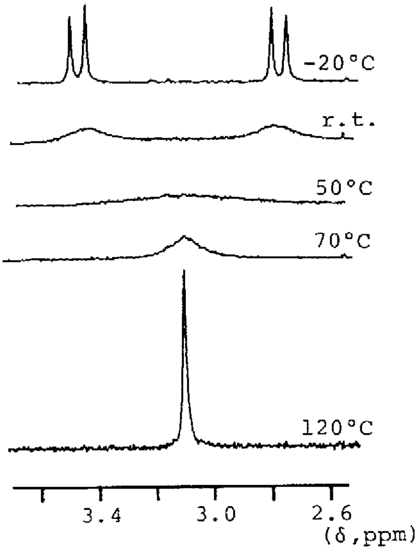
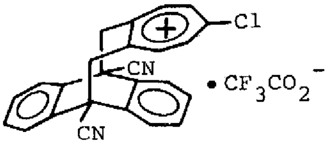


Fig.3. VT-NMR spectra of the methylene protons(Ha,Hb) of **3**.

for the concomitant inversion of the heptafulvene boat the flipping of the four carbon bridge has a higher free energy of activation ($\Delta G^{\ddagger}$= 14.8kcal/mol) than does **1** ($\Delta G^{\ddagger}$= 10.1kcal/mol).

Since it is well known that heptafulvene gives tropylium ion when treated with a protic acid, a drop of CF_3CO_2H was added to a $CDCl_3$ solution of **3**, and the reaction was monitored by the change in ^{1}H-NMR signal. Weakening of the vinylic signal intensity and a gradual increase of the AB quartet in the aromatic region was observed. At the same time a new sharp singlet at 3.90ppm appeared, upon decay of the broad methylene signals. The formation of tropylium ion from 3 is quite slow and after 10hrs, signals due to **3** completely disappeared, and new signals reached their maximum intensities, suggesting a quantitative conversion from **3** to tropylium ion species(**5**). When quenched with water, **5** gave **1c** quantitatively. These observations indicate that one could easily convert epoxide(**2c**) to **1c** in good yield.



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3) New compound gave satisfactory elemental analysis. Some of its physical properties are as follows:
3: m.p. 293°C; MS, m/z 380(M^++2), 378(M^+); IR(KBr) 1585, 1475, 1442, 995, 755 cm^{-1}; UV(cyclohexane) λmax(log ε), 301(4.48), 248(5.32), 208(6.56) nm; ^{1}H-NMR(δ,$CDCl_3$,270MHz), 2.82(1H,brs), 3.48(1H,brs), 5.48(1H,d,J=7.3Hz), 5.75(1H,d,J=1.5Hz), 5.80(1H,dd,J=10.7,1.5Hz), 6.09(1H,dd,J=10.7,2.0Hz), 6.17(1H,dd,J=7.3,2.0Hz), 7.40-7.55(4H,m), 7.88(4H,br).

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