Molecular Structure of [4](2,7)Benzo[*d*]troponophane

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An attractive molecular system for the evaluation of ring strain has been the series of compounds [*n*](2,7)benzo-[*d*]troponophanes **1**[13,12,9→5 (and as assumed, 4)], first synthesized[1] in 1956 by double aldol condensation of phthalaldehyde and cycloalkanone C_{n+3} (later **1**[n=10][2]). By successive shortening of the polymethylene bridge the carbonyl group has been forced increasingly out of the plane of the tropone moiety, causing a corresponding reduction of conjugation in the tropone ring and imposing strain in the bent ring system. The change in physical properties through the series **1** was reflected in extensive studies by IR and UV spectroscopy,[1] half-wave reduction potential ($-E_{1/2}$),[3,1b] dipole moment,[4,1b] combustion calorimetry for estimation of delocalization energy,[5,1b] exaltation of molecular refraction ($\Delta[R]_D$),[4] and later by photoelectron spectroscopy[6] and proton magnetic resonance.[2] An X-ray structure analysis of **1**[5] has been carried out.[7]

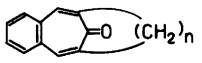
However, the condensation product of cycloheptanone and phthalaldehyde, isolated in 2.5 % yield, was tentatively assigned the structure **1**[4] solely from extrapolation of the trend in the change in physical properties through the higher homologues, **1**[5] to **1**[13], **1**[4], always terminating the various set of data as an extreme.

The decisive proof of the molecular structure of **1**[4], ($C_{15}H_{10}O$), is now given by the present X-ray crystallographic analysis. The crystal structure of **1**[4] will be discussed in relation to that of **1**[5] and of [4](2,7)troponophane.[8] Supplementary NMR and mass spectral data are given.

Experimental

1[4] was prepared as described,[1] recrystallized and finally sublimed at 90 °C/0.01 Torr. Crystal and experimental data are given in Table 1. Three test reflections were measured periodically at intervals of 135 intensity measurements during the data collection; a small systematic decrease in intensity was detected and corrected for. Corrections were also carried out for Lorentz and polarization effects but not for absorption and extinction. Unit cell dimensions were determined from the accurate setting angles for 25 reflections.

The coordinates of all non-hydrogen atoms were determined by direct methods.[9] Refinements were performed by least-squares calculations; hydrogen positions were calculated and included in the refinements with a constant isotropic thermal parameter ($B = 2.1$ Å^{-2}). In order to minimize the influence of the bonding electrons on the observed bond lengths the last refinement cycles included only re-



1[n]

Scheme 1.

Table 1. Crystal and experimental data for [4](2,7)-benzo[*d*]troponophane.

Compound	$C_{15}H_{10}O$
Diffractometer	SYNTEX *P*1
Radiation	Mo*K*α (λ = 0.71069 Å)
Crystal system	Monoclinic
a/Å	9.003(1)
b/Å	9.815(2)
c/Å	12.771(1)
β/°	98.97(1)
V/Å^3	1114.7(3)
T/K	123
Space group	$P2_1/c$
M	206.24
F(000)	432
Z	4
D_x/g cm^{-3}	1.229
Crystal size/mm	0.2×0.3×0.3
Scan mode	θ/2u
Scan speed (2θ)/°min^{-1}	4.0
Scan range (2θ)/°	1.6
Maximum sin (θ/λ)/Å^{-1}	0.90
Stability monitoring	3 Test refl./135 observ.
No. of indep. meas.	4278
No. with $I > 2.5\sigma(I)$	3910
Weighting scheme	$w = [\sigma^2(F)]^{-1}$
No. of parameters refined	163
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.038
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$	0.037
$S = [\Sigma w(F_o - F_c)^2 / (n - m)]^{1/2}$	1.54

Table 2. Fractional coordinates and equivalent isotropic thermal parameters[a] for **1**[4].

Atom	*x*	*y*	*z*	U_{eq}/Å^2
O1	1.19632(7)	0.13931(7)	0.83394(5)	0.0202
C1	1.12445(8)	0.22369(8)	0.87487(3)	0.0144
C2	1.05988(9)	0.35079(8)	0.82489(6)	0.0175
C3	0.90915(10)	0.36359(9)	0.804984(6)	0.0187
C4	0.80169(8)	0.26436(8)	0.83491(6)	0.0151
C5	0.82768(8)	0.18617(8)	0.92992(5)	0.0141
C6	0.96343(9)	0.20056(8)	1.00959(6)	0.0158
C7	1.10261(8)	0.22426(8)	0.98758(5)	0.0145
C8	0.65848(9)	0.25719(9)	0.77165(7)	0.0204
C9	0.54646(9)	0.17339(11)	0.79739(7)	0.0231
C10	0.57285(10)	0.09481(10)	0.88970(7)	0.0228
C11	0.71038(9)	0.10304(9)	0.95546(6)	0.0186
C12	1.17480(12)	0.46235(10)	0.82351(8)	0.0252
C131	1.20418(20)	0.45568(18)	0.91598(15)	0.0219
C132	1.23766(25)	0.49777(21)	0.94451(17)	0.0272
C141	1.25828(19)	0.43399(17)	1.02676(13)	0.0186
C142	1.32920(23)	0.38336(22)	1.00921(16)	0.0262
C15	1.23599(9)	0.28018(10)	1.06088(6)	0.0197

[a] $U_{eq} = 1/3\Sigma U_{ii}$.

Table 3. Bond lengths (Å) and bond angles (°) in the ordered part of **1**[4]. E.s.d. is 0.001 Å in bonds and 0.1 ° in angles.

Bond			Bond		
C1	C2	1.478	C1	C7	1.483
C2	C3	1.347	C6	C7	1.346
C3	C4	1.465	C5	C6	1.470
C4	C8	1.413	C5	C11	1.412
C8	C9	1.380	C10	C11	1.386
C4	C5	1.424	C9	C10	1.398
C2	C12	1.508	C7	C15	1.506
C1	O1	1.218			

Angle				Angle			
O1	C1	C2	126.0	O1	C1	C7	125.4
C1	C2	C12	113.2	C1	C7	C15	113.0
C1	C2	C3	118.5	C1	C7	C6	118.1
C3	C2	C12	127.1	C6	C7	C15	127.7
C2	C3	C4	125.1	C5	C6	C7	124.9
C3	C4	C5	123.6	C4	C5	C6	123.1
C3	C4	C8	117.7	C6	C5	C11	117.8
C5	C4	C8	118.3	C4	C5	C11	118.6
C4	C8	C9	122.0	C5	C11	C10	121.5
C8	C9	C10	119.7	C9	C10	C11	119.8
C2	C1	C7	108.3				

flections with sin θ/λ greater than 0.45 Å^{-1} (3134 reflections). Computer programs employed are described in Ref. 10. Final figures of merit are included in Table 1. Positional parameters are given in Table 2; lists of anisotropic thermal parameters, hydrogen coordinates and structure factors may be obtained from the authors upon request.

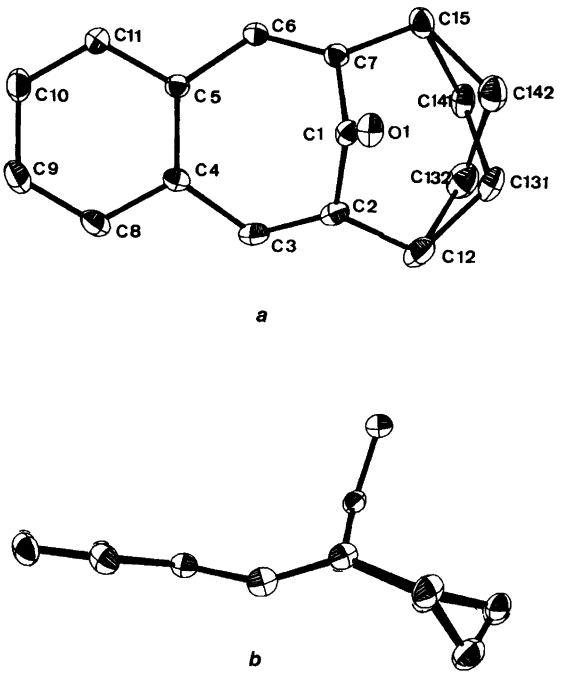


Fig. 1. ORTEP plot of [4](2,7)benzo[*d*]troponophane: (a) shows the structure and indicates the disorder; (b) is a projection onto the apparent mirror plane.

Description and discussion

An ORTEP plot of the structure of **1**[4] is shown in Fig. 1 where the numbering scheme is also indicated. The molecule consists of a benzene ring fused to a cycloheptatrienone moiety which is fused in a 1,3 manner to a cycloheptanone ring. The latter is disordered as visualised in Fig. 1(a), the molecule obtaining close to a non-crystallographic mirror plane. A projection of the molecule into this mirror plane is shown in Fig. 1(b). Bond lengths and angles of the ordered part of the molecule are given in Table 3; the disordered moiety is of course less accurate, the C–C bond lengths ranging from 1.52 Å to 1.60 Å for the C12–C13, C13–C14 and C14–C15 bonds. The apparent symmetry of the molecule is also reflected in the bond lengths and angles as given in Table 3.

Because of the close contact between the C1 atom and the carbon atoms across the cycloheptanone ring (the C1–C131 and C1–C142 distances are as short as 2.80 Å) the (4,5)benzotropone moiety is heavily strained. The tropone ring adopts a boat form in the same way as found for the **1**[5] molecule;[7] the present compound is, however, even more strained than the **1**[5]. Thus the dihedral angle between the bottom plane C2,C3,C6,C7 and the plane C1,C2,C7 is as large as 60.3° as compared with 51.3° in **1**[5], and the bottom plane forms an angle with the stern plane (C3,C4,C5,C6) of 29.7° as compared with 24.3° in **1**[5]. The corresponding values found for [4](2,7)troponophane, where a distortion of the tropone ring similar to that of the present compound is expected, are 61.5° and 28.9°, respectively. The angle between the bow plane and the C1–O1 double bond is 5.4° (towards the cycloheptanone ring) as compared with 6.5° in **1**[5][7] and 4.4° in [4](2,7)tropono-

phane.[8] Bond alternation in the tropone ring corresponds closely to that found for **1**[5].[7]

Selected characteristics of the ^{1}H NMR, ^{13}C NMR (DCl) and mass spectra are as follows (for comparison corresponding values for [4](2,7)troponophane[8] are given in brackets).

^{1}H NMR: $\delta_{3(6)}$ 6.574 (d) [6.21], protons in the benzene ring 7.25 (m), 7.49 (m); $\delta_{12(15)}$ 2.35 (m), 2.67 (m) [δ_α 2.26 (m), 2.68 (m)]; $\delta_{13(14)}$ 1.57 (m), 1.87 (m) [δ_β 1.36 (m), 1.79 (m)].

^{13}C NMR: $\delta_{2(7)}$ 135.7 [133.2]; $\delta_{3(6)}$ 121.2 [118.3], $C_{4(5)}$ 142.7 [129]; $\delta_{8(11)}$ 129.4; $\delta_{9(10)}$ 126.0; $\delta_{12(15)}$ 29.76 [δ_α 29.3]; $\delta_{13(14)}$ 26.6 [δ_β 25.8]; $\delta_{C=O}$ 206.3 [203.7].

Mass spectra (relative abundance above 15 % in parentheses): *m/z* 210 M^+ absent; 182 (100) ($M^+ - CO_2$ or $M - C_2H_2$), 181 (19), 167 (25), 165 (19), 154 (55), 153 (21), 152 (19), 141 (40).

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