

Structure of 9-Annulene Derivatives. 2. 7*H*-Benzocyclononen-7-one, C₁₃H₁₀O

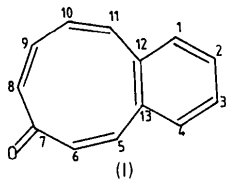
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Abstract. $M_r = 182.2$, orthorhombic, $P2_12_12_1$, $a = 8.643$ (6), $b = 9.653$ (2), $c = 11.802$ (2) Å, $U = 984.6$ Å³, $Z = 4$, $D_x = 1.22$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.082$ mm⁻¹, $F(000) = 384$, $T = 295$ K. Final $R = 0.032$ for 833 observed reflections. The strained nine-membered ring adopts a distorted tub conformation while the phenyl ring is planar. The molecules are packed by van der Waals interactions.

Introduction. In this paper, we continue our investigation of the structural properties of compounds containing a fully unsaturated nine-membered carbocyclic fragment by reporting the X-ray structure determination of the title compound (I).



Experimental. Suitable crystals of (I) grown at room temperature from an ether solution. Crystal dimensions $0.30 \times 0.35 \times 0.90$ mm. Enraf-Nonius CAD-4 diffractometer, take-off angle 5° , graphite-crystal-monochromatized Mo $K\alpha$ radiation. Cell dimensions obtained by least-squares refinement of setting angles of 25 accurately centred large-angle ($\theta \leq 20^\circ$) reflections. 1659 independent reflections (to $\theta \leq 30^\circ$) measured using ω - 2θ scans, background scans being taken on each side of peaks. Range of hkl : 0–12, 0–13, 0–16. Intensities of three standard reflections showed no significant variation during data collection. Structure solved by direct methods, an E map generated by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) correctly locating all non-H atomic positions. 833 reflections considered observed, with $I \geq 3\sigma(I)$, only these used in subsequent steps. $R_{\text{int}} = 0.020$. Three cycles of full-matrix least-squares refinement (*SHELX76*, Sheldrick, 1976) with isotropic temperature factors gave $R = 0.122$, incorporation of anisotropic temperature factors reduced R to 0.072. All

H atoms located at this stage from a difference map and further refinement of non-H atoms anisotropically and H atoms isotropically reduced R to 0.038. No absorption correction deemed necessary, but refinement of an empirical extinction coefficient [$F_{\text{corr}}^2 = F(1 - 1.84 \times 10^{-6} F^2 / \sin \theta)$] caused a significant reduction in R to 0.032. Weighting scheme based on counting statistics used, $w = 1.55 / (\sigma^2 |F_o| + 3.47 \times 10^{-4} F_o^2)$ minimizing $\sum w \Delta F^2$; $R_w = 0.034$, $S = 5.18$. $\Delta/\sigma = 0.006$. Final difference map showed no peaks or depressions larger than $0.15 \text{ e } \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the least-squares plane of the molecule in isometric projection, with 20% probability ellipsoids for the non-H atoms and arbitrary spheres of radius 0.05 Å for H atoms. Fig. 2 shows the packing arrangement. Both figures were produced using *ORTEP* (Johnson, 1976). Table 1 lists the fractional atomic coordinates and Table 2 lists bond distances and angles together with the endocyclic torsion angles for the nine-membered ring.†

The nine-membered ring adopts a distorted tub arrangement which, allowing for the constraints imposed by the carbonyl group, shows close similarities to the 9-annulene which was the subject of Part 1 of this series of papers (Mazhar-ul-Haque, Ahmed & Horne, 1983). Thus, excluding the singly bonded C–C–C segment, the r.m.s. difference between the corresponding internal angles of the respective nine-membered rings is 2.8° , and between the endocyclic torsion angles 7.2° . In addition, given the strained nature of the ring, which is reflected in the expanded internal ring angles, the localized C–C double-bond lengths in both compounds are rather short [mean value 1.320 (5) Å for the annulene and 1.310 (5) Å for the annulenone].

Analysis of the thermal-motion tensors in terms of a rigid-body model (Schomaker & Trueblood, 1968)

† Lists of coordinates and bond lengths and angles involving H atoms, together with structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38708 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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results in significant disagreement between the observed and calculated tensor components [$\langle(\Delta U_{ij}^2)\rangle^{1/2} = 0.0064 \text{ \AA}^2$, $\langle\sigma(U_{ij})\rangle = 0.0019 \text{ \AA}^2$], primarily due to internal motion at the O atom. [Omission of the O atom from the rigid-body treatment reduces $\langle(\Delta U_{ij}^2)\rangle^{1/2}$ to 0.0027 \AA^2 .] Bond lengths corrected for libration on the basis of a rigid body comprising all the non-H atoms are listed in Table 2. Librational corrections to the bond angles are negligible.

The phenyl ring is planar, with a mean bond length of $1.383(5) \text{ \AA}$.

The intermolecular packing arrangement is determined by normal van der Waals contacts, with no interactions between the non-H atoms involving contact distances of less than 3.5 \AA .

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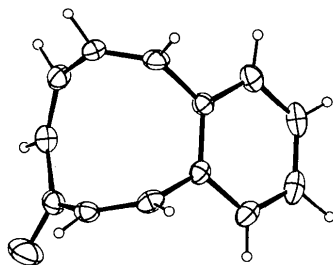


Fig. 1. View of the molecule.

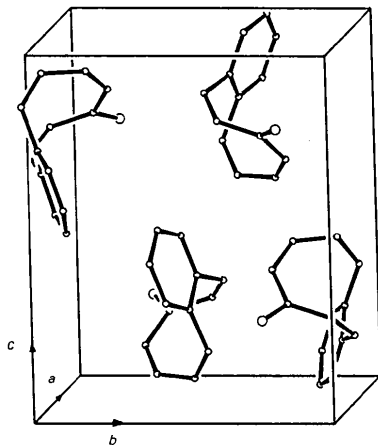


Fig. 2. The molecular packing arrangement.

Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic U values ($\times 10^3$) for non-H atoms

	$U_{eq} = \frac{1}{3}(\text{trace of the } U_{ij} \text{ matrix}).$			$U_{eq} (\text{\AA}^2)$
	x	y	z	
C(1)	6954 (3)	3998 (3)	2858 (3)	65
C(2)	7152 (5)	3524 (3)	3949 (3)	75
C(3)	5962 (5)	3625 (3)	4711 (3)	76
C(4)	4572 (4)	4186 (3)	4392 (2)	64
C(5)	2857 (3)	5297 (3)	2961 (2)	59
C(6)	1755 (3)	4733 (3)	2358 (2)	58
C(7)	1698 (3)	3284 (3)	1972 (2)	61
C(8)	2783 (3)	2626 (3)	1187 (3)	61
C(9)	3902 (3)	3163 (4)	564 (3)	66
C(10)	4617 (3)	4525 (4)	526 (2)	64
C(11)	5366 (4)	5111 (3)	1353 (2)	63
C(12)	5559 (3)	4563 (3)	2516 (2)	52
C(13)	4346 (3)	4650 (2)	3287 (2)	50
O	584 (3)	2596 (3)	2279 (3)	112

Table 2. Molecular geometry

(a) Lengths (\AA)					
	Observed	Corrected		Observed	Corrected
C(2)–C(1)	1.377 (5)	1.386	C(9)–C(8)	1.322 (4)	1.333
C(12)–C(1)	1.383 (3)	1.391	C(8)–C(7)	1.463 (4)	1.474
C(3)–C(2)	1.370 (5)	1.381	O – C(7)	1.223 (3)	1.233
C(4)–C(3)	1.370 (5)	1.378	C(10)–C(9)	1.453 (4)	1.464
C(13)–C(4)	1.393 (3)	1.402	C(11)–C(10)	1.301 (4)	1.307
C(6)–C(5)	1.308 (4)	1.315	C(12)–C(11)	1.481 (4)	1.490
C(13)–C(5)	1.481 (4)	1.490	C(13)–C(12)	1.390 (3)	1.401
C(7)–C(6)	1.472 (4)	1.483			
(b) Angles ($^\circ$)					
C(12)–C(1)–C(2)	120.8 (3)		C(9)–C(8)–C(7)	130.7 (3)	
C(3)–C(2)–C(1)	119.8 (3)		C(11)–C(10)–C(9)	125.6 (3)	
C(4)–C(3)–C(2)	120.4 (3)		C(12)–C(11)–C(10)	126.6 (3)	
C(13)–C(4)–C(3)	120.5 (3)		C(11)–C(12)–C(1)	120.6 (2)	
C(13)–C(5)–C(6)	126.7 (3)		C(13)–C(12)–C(1)	119.4 (2)	
C(7)–C(6)–C(5)	126.1 (3)		C(13)–C(12)–C(11)	120.0 (2)	
C(8)–C(7)–C(6)	126.0 (2)		C(5)–C(13)–C(4)	120.0 (2)	
O – C(7)–C(6)	116.7 (3)		C(12)–C(13)–C(4)	119.2 (2)	
O – C(7)–C(8)	117.1 (3)		C(12)–C(13)–C(5)	120.7 (2)	
C(10)–C(9)–C(8)	133.1 (3)				
(c) Endocyclic torsion angles for the nine-membered ring ($^\circ$)					
C(12)–C(13)–C(5)–C(6)	78.5 (5)		C(8)–C(9)–C(10)–C(11)	61.8 (7)	
C(13)–C(5)–C(6)–C(7)	6.5 (6)		C(9)–C(10)–C(11)–C(12)	–4.3 (6)	
C(5)–C(6)–C(7)–C(8)	–63.9 (6)		C(10)–C(11)–C(12)–C(13)	–77.0 (6)	
C(6)–C(7)–C(8)–C(9)	–8.6 (7)		C(11)–C(12)–C(13)–C(5)	–0.5 (5)	
C(7)–C(8)–C(9)–C(10)	–9.8 (8)				

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