

Table 3. Bond angles ($^{\circ}$) ($\sigma = 0.2-0.4^{\circ}$ for C-C-C, C-C-O, $1.4-2.3^{\circ}$ for C-C-H, O-C-H, H-C-H)

C(11)-C(10)-C(9)	125.3	C(10)-C(9)-C(8)	125.2
C(1)-C(11)-C(10)	125.0	C(7)-C(8)-C(9)	123.8*
C(11)-C(1)-C(12)	117.5	C(8)-C(7)-C(12)	117.7
C(2)-C(1)-C(11)	121.9	C(6)-C(7)-C(8)	120.1*
C(2)-C(1)-C(12)	120.3	C(6)-C(7)-C(12)	121.2*
C(1)-C(2)-C(3)	129.1	C(5)-C(6)-C(7)	129.3
C(2)-C(3)-C(4)	128.4	C(6)-C(5)-C(4)	128.6
C(2)-C(3)-C(13)	114.7	C(6)-C(5)-C(14)	114.4
C(4)-C(3)-C(13)	116.9	C(4)-C(5)-C(14)	117.0
C(3)-C(4)-C(5)	116.3		
C(1)-C(12)-C(7)	102.4		
C(3)-C(13)-O(1)	125.5	C(5)-C(14)-O(2)	126.2
C(9)-C(10)-H(10)	117.5	C(10)-C(9)-H(9)	119.1
C(11)-C(10)-H(10)	116.0	C(8)-C(9)-H(9)	114.2
C(10)-C(11)-H(11)	118.8	C(9)-C(8)-H(8)	120.0
C(1)-C(11)-H(11)	115.8	C(7)-C(8)-H(8)	116.1
C(1)-C(12)-H(12A)	112.2	C(7)-C(12)-H(12A)	114.3
C(1)-C(12)-H(12B)	111.6	C(7)-C(12)-H(12B)	108.5
C(1)-C(2)-H(2)	115.2	C(7)-C(6)-H(6)	113.0
C(3)-C(2)-H(2)	115.4	C(5)-C(6)-H(6)	117.0
C(3)-C(4)-H(4A)	104.7	C(5)-C(4)-H(4A)	110.4*
C(3)-C(4)-H(4B)	109.7	C(5)-C(4)-H(4B)	113.9*
C(3)-C(13)-H(13)	120.2	C(5)-C(14)-H(14)	109.2*
O(1)-C(13)-H(13)	114.2	O(2)-C(14)-H(14)	124.7*
H(12B)-C(12)-H(12A)	107.8		
H(4B)-C(4)-H(4A)	100.3		

* The difference between the values for these pairs is equal to or greater than 3σ .

Table 4. Selected intermolecular contacts (\AA)

	Symmetry operation applied to second atom	
C(9)···C(9)	$-\frac{1}{2} - x, \frac{1}{2} - y, z$	3.360 (6)
C(11)···H(4B)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	2.87 (3)
O(1)···H(4B)	$\frac{1}{2} - x, \frac{1}{2} - y, z$	2.58 (3)
O(1)···H(6)	$\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$	2.48 (3)
O(2)···H(8)	$\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$	2.59 (3)
O(2)···H(13)	$\frac{1}{2} - x, y, \frac{1}{2} + z$	2.37 (3)

The packing within the unit cell (see Table 4) is responsible for the asymmetry of ALD. In particular, the O atoms of the two formyl groups are involved in four short intermolecular contacts of the type O···H

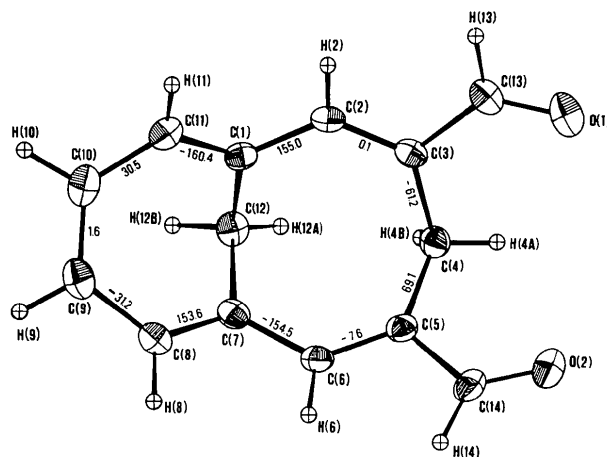


Fig. 1. A drawing of the molecule showing the numbering scheme and torsion angles ($^{\circ}$) along the perimeter ring. Thermal ellipsoids are at the 20% probability level. H atoms are on an arbitrary scale. The signs of the torsion angles follow the convention proposed by Klyne & Prelog (1960).

that have not been found in DIAL. The two C-O bonds are in positions *trans* to their nearest double bonds for steric reasons.

The alternation of short and long bonds along the perimeter ring indicates an open 14π -electron system. As expected, the variation of bond lengths decreases on going from the outer to the central part of the π system.

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Structure of 1,6-Methano[10]annulene

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Abstract. $C_{11}H_{10}$, orthorhombic, $Fdd2$, $a = 33.9690$ (39), $b = 15.1117$ (13), $c = 6.1811$ (6) \AA , $Z = 16$, $D_c = 1.191$ (145 K), $D_m = 1.129$ Mg m^{-3}

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(floatation at 291 K), $\mu(\text{Mo } K\alpha) = 0.073$ mm^{-1} , $F(000) = 1216$. The structure was solved by a constrained least-squares method and refined to $R = 0.051$ for 1210

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observed reflexions. The perimeter is non-planar, with bond lengths in the range 1.373 (3)–1.419 (4) Å, confirming the aromaticity of the 10 π -electron system. The transannular distance C(1)···C(6) is 2.235 (3) Å.

Introduction. The synthesis and properties of the title compound (hereafter MANN) were discussed by Vogel (1968), who recently supplied us with a sample for the structural analysis, carried out at low temperature (145 K) because of the low melting point (302 K). Cell dimensions were obtained by measuring the setting angles of 48 reflexions on the diffractometer, and refined by the least-squares method. Intensities were collected from a spherical crystal (diameter 0.4 mm) on a Syntex computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the θ - 2θ scan technique. Two equivalent sets of intensities were measured up to $2\theta = 60^\circ$. Cooling of the crystal was by a cold nitrogen-gas stream obtained by a Syntex LT-1 low-temperature device. After averaging, 1266 independent reflexions remained. Of these, 1210 were considered observed with $I > 0$ and used in subsequent calculations. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved with a molecular model derived from the structure of 11,11-difluoro-1,6-methano[10]annulene (DIF; Pilati & Simonetta, 1976) and a constrained least-squares procedure reported by Bianchi, Gramaccioni, Pilati & Simonetta (1980). The structure was refined with a modified version of ORFLS (Busing, Martin & Levy, 1962), with as

Table 1. Atomic coordinates and equivalent isotropic thermal parameters

Fractional coordinates are multiplied by 10^5 for heavy atoms, by 10^4 for hydrogen atoms. The equivalent isotropic parameter is taken as $B (\text{\AA}^2) = \frac{1}{3}(\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j)$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B
C(1)	41557 (5)	22769 (12)	-5033	1.68 (5)
C(2)	43123 (6)	14478 (13)	481 (48)	2.06 (7)
C(3)	45167 (6)	9275 (12)	-14010 (49)	2.23 (7)
C(4)	47050 (6)	12038 (13)	-33309 (48)	2.12 (7)
C(5)	47223 (6)	20531 (13)	-41388 (47)	1.97 (6)
C(6)	44533 (5)	27133 (12)	-35460 (43)	1.70 (5)
C(7)	45347 (6)	36243 (13)	-33441 (48)	2.13 (6)
C(8)	43582 (6)	41485 (13)	-18049 (49)	2.28 (7)
C(9)	41697 (6)	38716 (14)	1293 (46)	2.15 (7)
C(10)	41225 (6)	30195 (14)	8526 (47)	2.00 (6)
C(11)	40585 (5)	24145 (14)	-28252 (43)	1.82 (5)
H(2)	4303 (6)	1252 (14)	1519 (45)	4.1 (5)
H(3)	4595 (6)	342 (14)	-905 (40)	4.0 (5)
H(4)	4886 (6)	777 (14)	-3883 (42)	4.0 (5)
H(5)	4932 (7)	2218 (14)	-4969 (43)	4.5 (5)
H(7)	4733 (6)	3868 (13)	-4263 (39)	3.7 (4)
H(8)	4414 (6)	4772 (15)	-1854 (42)	4.3 (5)
H(9)	4119 (6)	4330 (13)	1136 (39)	3.8 (5)
H(10)	4100 (6)	2930 (14)	2366 (49)	4.3 (5)
H(11A)	3862 (5)	2850 (12)	-3022 (32)	2.9 (4)
H(11B)	3984 (6)	1856 (13)	-3569 (40)	3.8 (5)

starting parameters the atomic coordinates of the solution and the scale and the overall temperature factors of the Wilson plot. Least-squares refinement minimizing $\sum w ||F_o| - |F_c||^2$ with C and H atoms having anisotropic and isotropic temperature factors, respectively, converged to $R = 0.051$ for 1210 observed data. A final difference map was featureless, with a maximum peak of 0.22 e \AA^{-3} .

Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for C atoms from Cromer & Waber (1965). The final atomic coordinates are listed in Table 1.*

Discussion. The atom numbering and bond distances are shown in Fig. 1(a); bond angles are reported in Table 2.

The molecular symmetry of MANN is within 3σ of $mm2$, except for the angles C(7)–C(8)–C(9) [$127.6 (2)^\circ$] and C(3)–C(4)–C(5) [$126.8 (2)^\circ$].

The values of the bond lengths along the ring indicate the aromatic character of the annulene system; these also show small systematic variations. This

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35421 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

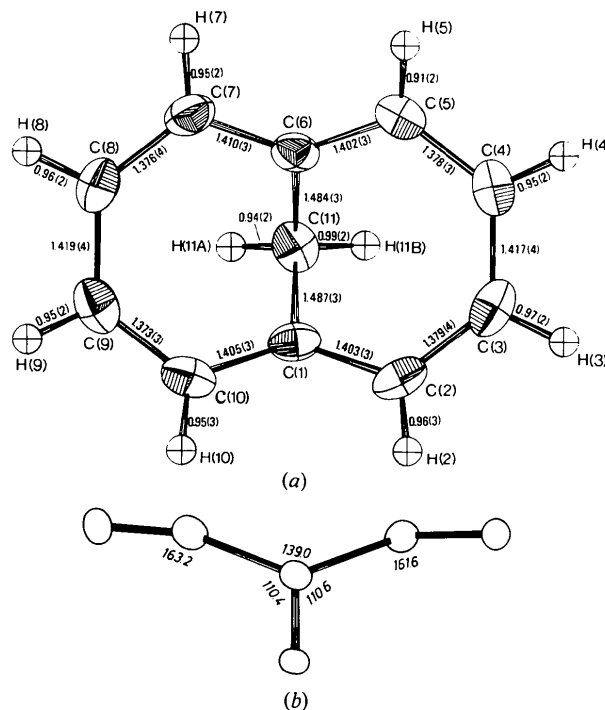


Fig. 1. A molecule of MANN viewed along a principal axis of inertia. (a) Numbering scheme and bond lengths (Å). (b) Angles ($^\circ$) between least-squares planes.

Table 2. Bond angles ($^{\circ}$) ($\sigma = 0.2^{\circ}$ for C—C—C, $1.2-1.6^{\circ}$ for C—C—H, H—C—H)

C(8)—C(9)—C(10)	127.1	C(9)—C(8)—C(7)	127.6
C(9)—C(10)—C(1)	123.1	C(8)—C(7)—C(6)	122.6
C(10)—C(1)—C(2)	126.8	C(7)—C(6)—C(5)	126.2
C(10)—C(1)—C(11)	116.5	C(7)—C(6)—C(11)	116.6
C(2)—C(1)—C(11)	116.3	C(5)—C(6)—C(11)	116.8
C(1)—C(2)—C(3)	122.8	C(6)—C(5)—C(4)	122.7
C(2)—C(3)—C(4)	127.3	C(5)—C(4)—C(3)	126.8
C(1)—C(11)—C(6)	97.6		
C(8)—C(9)—H(9)	114.8	C(9)—C(8)—H(8)	113.9
C(10)—C(9)—H(9)	116.8	C(7)—C(8)—H(8)	117.2
C(9)—C(10)—H(10)	117.7	C(8)—C(7)—H(7)	119.8
C(1)—C(10)—H(10)	118.8	C(6)—C(7)—H(7)	117.5
C(1)—C(11)—H(11A)	112.2	C(6)—C(11)—H(11A)	112.8
C(1)—C(11)—H(11B)	112.6	C(6)—C(11)—H(11B)	110.6
C(1)—C(2)—H(2)	119.6	C(6)—C(5)—H(5)	117.5
C(3)—C(2)—H(2)	117.2	C(4)—C(5)—H(5)	119.4
C(2)—C(3)—H(3)	116.8	C(5)—C(4)—H(4)	118.2
C(4)—C(3)—H(3)	114.2	C(3)—C(4)—H(4)	113.2
H(11A)—C(11)—H(11B)	110.6		

alternation is correlated to the deviation from planarity of the perimeter ring (Fig. 1b). The strain introduced by the methano bridge leads to bond-angle distortions (Table 2). The maximum absolute value of the torsion

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Isopropylammoniomethanesulfonate

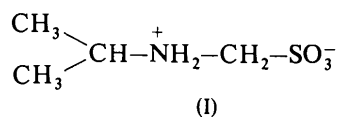
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(Received 10 April 1980; accepted 23 July 1980)

Abstract. $C_4H_{11}NO_3S$, monoclinic, $P2_1/n$, $a = 10.458$ (6), $b = 5.698$ (3), $c = 12.794$ (6) Å, $\beta = 112.44$ (4) $^{\circ}$, $M_r = 153.20$, $Z = 4$, $D_m = 1.43$ (floatation), $D_x = 1.444$ Mg m $^{-3}$, $\mu(\text{Mo } K\alpha) = 0.39$ mm $^{-1}$. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The final R was 0.056 for 1039 measured reflections. The ammonium group of one molecule is hydrogen-bonded to O(1) and O(3) belonging to the sulfonate groups of molecules related to it by the twofold screw axis.

Introduction. Crystals of (I) were kindly provided by Professor R. A. M. C. De Groote of the Chemistry and Molecular Physics Department, Institute of Physics and Chemistry of São Carlos.



This structure determination has been undertaken to study the hydrogen-bonding scheme in this zwitterion

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angles τ along the ring is 35.6 (3) $^{\circ}$ (if $|\tau| > 90^{\circ}$, it is replaced by $180 - |\tau|$).

The intramolecular distance C(1)···C(6) is 2.235 (3) Å, slightly shorter than the corresponding 2.269 (5) Å found in DIF. The three shortest intermolecular contacts, ranging from 2.82 (3) to 2.89 (2) Å, are between C and H atoms. The remaining intermolecular distances are consistent with normal van der Waals packing radii.

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which was obtained during an investigation of amino-methanesulfonate derivatives of aliphatic compounds.

A crystal of approximate dimensions $0.4 \times 0.5 \times 0.6$ mm was used for the data collection on a CAD-4 diffractometer. The cell parameters were refined from the setting angles for 25 reflections. Three-dimensional intensities were collected using graphite-monochromated Mo $K\alpha$ radiation up to $2\theta = 60^{\circ}$. The ω - 2θ scanning mode with varying interval was used. Of the 1267 recorded independent reflections, 1039 were observed above background [$I > 2\sigma(I)$, where $\sigma(I)$ was based on counting statistics]. The data were reduced to structure factors without absorption correction.

The structure was solved by application of *MULTAN* (Germain, Main & Woolfson, 1971) to the 162 reflections with $E > 1.50$. All the non-hydrogen atoms appeared clearly on the E map based on the set of phases giving the highest combined figure of merit. All the H atoms were placed at their calculated positions.

Refinement was carried out by full-matrix least-squares. © 1980 International Union of Crystallography