

*Acta Cryst.* (1975). B31, 1207**15,16-Dimethyl-1,6:8,13-ethanediylidene[14]annulene**

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**Abstract.** C<sub>18</sub>H<sub>16</sub>, hexagonal, space group  $P6_3/m$ ;  $a = 11.213$  (2),  $c = 17.855$  (3) Å,  $Z = 6$ ,  $D_o = 1.184$ ,  $D_c = 1.190$  g cm<sup>-3</sup>. The parameters were refined by full-matrix least-squares calculations to an  $R$  of 0.07 for 901 counter reflexions. The annulene ring is nearly planar with bond lengths very close to the aromatic value.

**Introduction.** The centrosymmetric space group  $P6_3/m$  was chosen according to the extinctions and intensity statistics, and confirmed by the structure solution. Cell constants were obtained by a least-squares fit of the  $2\theta$  values for 27 reflexions for  $\lambda = 1.5418$  Å. The density was measured by flotation in K<sub>2</sub>HgI<sub>4</sub> solution. Intensities were measured on a Syntex  $P\bar{T}$  automatic diffractometer with Cu  $K\alpha$  radiation monochromated by a graphite crystal. All independent reflexions with  $2\theta \leq 140^\circ$  (Cu radiation) were collected by the  $\theta$ - $2\theta$  scan technique, the scan speed varying from 1 to 12° min<sup>-1</sup> (depending on the intensity) and the scan range from 1° below the  $\alpha_1$  peak to 1.1° above the  $\alpha_2$  peak. The background count was recorded for half the total scan time on each side of the scan range. Two standard reflexions were measured after every 40 reflexions; no significant change in intensity was revealed.

1254 independent reflexions were measured, of which 902 with  $I \geq 0$  were considered 'observed'. Each reflexion was given a variance  $\sigma^2(I)$  based on counting statistics plus a term  $(0.02 S)^2$ , where  $S$  is the scan count (Peterson & Levy, 1957). The data were corrected for Lorentz and polarization factors but not for absorption ( $\mu_{Cu K\alpha} = 5.13$  cm<sup>-1</sup>).

The structure was solved by determining the orientation and the position of a molecular model in the cell. The model was constructed by the same procedure as

for 1,6:8,13-propane-1,3-diylidene[14]annulene (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972). Molecular symmetry  $mm2$  was assumed with the two-fold axis coincident with the  $x_0$  axis of a right-handed Cartesian coordinate system and the elongation direction of the molecule parallel to  $z_0$ . Since the value of  $Z$  reduced the asymmetric unit to one half of a molecule, the crystallographic symmetry plane at  $z = \frac{1}{4}$  was assumed to be coincident with the molecular  $m$ -symmetry plane containing C(7) and C(14). Orientations were given to the model by rotation around  $z_0$  from 0 to 360° at intervals of 7.5°. Each oriented model was then shifted along  $x$  and  $y$  (the explored region was  $0 - a$  along  $x$  and  $0 - \frac{1}{2}b$  along  $y$  at intervals of 0.03) while comparing observed and calculated structure factors for a sample of low-order reflexions ( $\sin^2 \theta / \lambda^2 \leq 0.07$ ). The lowest  $R$  (0.18) indicated the orientation and the position of the asymmetric unit. After four cycles of full-matrix least-squares adjustment of the coordinates and isotropic temperature factors, a difference map showed the location of the hydrogen atoms. Final refinement was performed by full-matrix least-squares calculations on scale factor, extinction parameter [Zachariasen, 1963; Larson, 1967, equation (3); Kerr & Ashmore, 1974, equation (5)], anisotropic C and isotropic H atoms by minimizing the function  $\sum w(|F_o| - |F_c|)^2$  with weights  $w = 1/\sigma^2(F)$ . All measured reflexions were included, with the exception of one (marked by an asterisk in the structure-factor table) which is probably affected by some observational error. The final  $R$  ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.07, and the goodness of fit  $\{ = [\sum w(\Delta F)^2 / (n - p)]^{1/2} \}$  for  $n = 901$  observations and  $p = 120$  parameters, 1.77. The largest shift in the final cycle was 0.11σ. A final difference map showed a maximum value of 0.18 e Å<sup>-3</sup>.

Table 1. Fractional coordinates and thermal parameters with standard deviations

Values for the non-hydrogen atoms are  $\times 10^4$ . Hydrogen atom positional parameters are  $\times 10^3$ . The thermal parameters are of the form  $\exp[-(B_{11}h^2 + 2B_{12}hk + \dots)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	-570 (2)	2012 (2)	1858 (1)	75 (2)	92 (2)	54 (1)	41 (2)	5 (1)	-8 (1)
C(2)	-917 (3)	1542 (3)	1122 (2)	112 (3)	147 (4)	63 (2)	46 (3)	8 (2)	-17 (2)
C(3)	-989 (3)	2252 (4)	518 (2)	143 (4)	229 (6)	53 (2)	37 (4)	11 (2)	1 (3)
C(4)	-1026 (3)	3477 (4)	518 (3)	151 (4)	243 (7)	63 (2)	34 (4)	5 (2)	46 (3)
C(5)	-1024 (3)	4247 (4)	1120 (3)	137 (4)	165 (5)	82 (2)	60 (3)	1 (2)	47 (3)
C(6)	-649 (2)	4160 (2)	1855 (2)	99 (3)	84 (3)	68 (1)	42 (2)	1 (2)	20 (2)
C(7)	-1032 (3)	4564 (3)	2500 (0)	107 (4)	94 (4)	89 (3)	63 (4)	0 (0)	0 (0)
C(14)	-914 (3)	1230 (3)	2500 (0)	79 (3)	69 (3)	69 (2)	38 (3)	0 (0)	0 (0)
C(15)	222 (2)	3527 (2)	2063 (1)	68 (2)	78 (2)	55 (1)	31 (2)	6 (1)	5 (1)
C(17)	1637 (3)	4281 (3)	1680 (2)	84 (3)	136 (3)	76 (2)	31 (3)	14 (2)	7 (2)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(1)	-118 (2)	57 (3)	104 (1)	8.9 (7)
H(2)	-115 (3)	182 (3)	0 (2)	12.1 (10)
H(3)	-121 (3)	373 (3)	1 (2)	11.5 (9)
H(4)	-133 (3)	490 (3)	103 (2)	12.3 (10)
H(5)	-159 (3)	497 (3)	250 (0)	9.0 (10)
H(10)	-143 (3)	24 (3)	250 (0)	8.5 (9)
H(11)	152 (3)	424 (3)	110 (2)	10.6 (9)
H(12)	220 (3)	388 (2)	184 (1)	9.4 (8)
H(13)	212 (2)	529 (3)	185 (1)	9.5 (7)

Table 2. Bond lengths (Å)

	Observed	Corrected*
C(1)—C(14)	1.375	1.384
C(6)—C(7)	1.381	1.390
C(1)—C(2)	1.398	1.407
C(5)—C(6)	1.396	1.405
C(2)—C(3)	1.367	1.376
C(4)—C(5)	1.378	1.387
C(3)—C(4)	1.394	1.404
C(1)—C(15)	1.517	1.525
C(6)—C(15)	1.513	1.523
C(15)—C(16)	1.560	1.570
C(15)—C(17)	1.537	1.543

\* For thermal libration.

Table 3. Bond angles (°) involving the ethane bridge

C(1)—C(15)—C(17)	111.9	C(6)—C(15)—C(16)	104.2
C(6)—C(15)—C(17)	111.4	C(1)—C(15)—C(6)	108.2
C(1)—C(15)—C(16)	104.0	C(16)—C(15)—C(17)	116.5

Refinement of the structure was performed with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors for C were from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). The final value of the extinction parameter *g* [Larson, 1967, equation (3)] was  $2.3 \times 10^{-6}$ . The final atomic parameters are in Table 1.\* Bond lengths, uncorrected and corrected for thermal libration (Schomaker & Trueblood, 1968; program written by Filippini & Gramaccioli, 1969) are in Table 2. Bond angles involving the ethane bridge are in Table 3, the remaining bond angles being in Fig. 1, with dihedral and torsion angles. Mean values of the e.s.d.'s for bond angles and torsion angles involving only C atoms are 0.004 Å, 0.26° and 0.6° respectively; for C—H bonds they are 0.03 Å and for angles involving H atoms about 2°.

**Discussion.** This determination was undertaken as a continuation of previous studies of bridged [14]annul-

enes. It is well known that the chemical behaviour of these compounds is closely related to the distortion imposed by the bridges upon the annulene ring. In fact the olefinic reactivity of 7-methoxycarbonyl-*anti*-1,6:8,13-dimethano[14]annulene is connected with the systematic succession of long and short bond distances found in the annulene perimeter (Gramaccioli, Mimun, Mugnoli & Simonetta, 1973). On the other hand the C—C distances found for 1,6:8,13-butane-1,4-diylidene-[14]annulene (Gramaccioli, Mugnoli, Pilati & Simonetta, 1972), 1,6:8,13-propane-1,3-diylidene[14]annulene (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972) and 1,6:8,13-cyclopropanediylidene[14]annulene (Mugnoli & Simonetta, 1974) agree with the aromatic character of these compounds.

The situation for 15,16-dimethyl-1,6:8,13-ethane-diylidene[14]annulene is very close to that of the latter compounds. The C—C lengths in the annulene ring range from 1.376 to 1.407 Å (values corrected for thermal libration; mean 1.393 Å) and the annulene perimeter is nearly planar, the largest distance for a perimeter atom from the least-squares plane C(2), C(5), C(9), C(12) being 0.35 Å. Torsion angles in the annulene ring show that the largest misalignment angle between the directions of adjacent *p<sub>z</sub>* carbon orbitals is 23°. It may be concluded that the geometry of the title compound is consistent with its aromatic reactivity (Vogel, 1974).

C—H lengths are in the range 0.94–1.01 Å. The shortest intermolecular contacts are between C(4) in

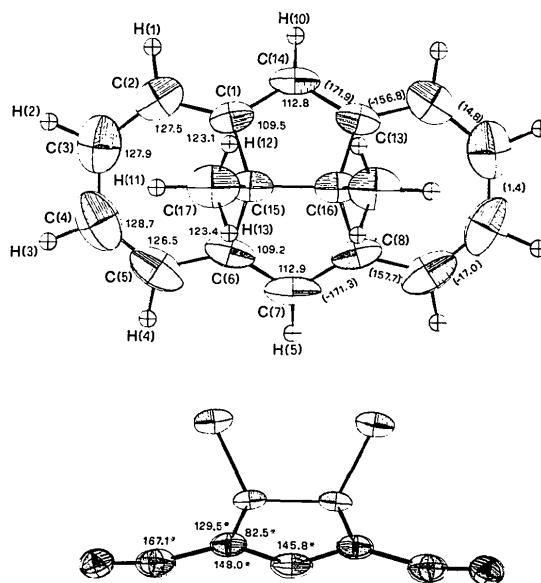


Fig. 1. One molecule of the title compound viewed along two principal axes of inertia. Bond angles are shown. Values in parentheses refer to torsion angles, starred values to dihedral angles. Thermal ellipsoids (Johnson, 1965) for carbon atoms are drawn at probabilities of 0.40 and 0.20 in the upper and lower parts respectively. Hydrogen atoms are on an arbitrary scale.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30819 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$x, y, z$  and C(4) in  $-x, 1-y, -z$  (3.54 Å), C(14) in  $x, y, z$  and H(10) in  $y-x, -x, z$  (2.79 Å), H(2) in  $x, y, z$  and H(11) in  $x-y, x, -z$  (2.55 Å).

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### 1,3-Dimethyl-2,4-bis(trichlormethyl)-2,2,4,4-tetrafluor-1,3-diaza-2,4-diphosphetidin

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**Abstract.** [(Cl<sub>3</sub>C)<sub>2</sub>F<sub>2</sub>PNCH<sub>3</sub>]<sub>2</sub>, triclinic,  $P\bar{1}$ ,  $a = 7.416$  (6),  $b = 8.377$  (4),  $c = 6.308$  (3) Å,  $\alpha = 109.83$  (4),  $\beta = 103.37$  (5),  $\gamma = 86.53$  (5)°,  $M = 432.80$ ,  $Z = 1$ ,  $D_x = 2.00$  g cm<sup>-3</sup>. The molecule is centrosymmetric with trigonal coordination at nitrogen and trigonal-bipyramidal coordination at phosphorus. A long equatorial P–C bond of 1.888 (5) Å and wide N<sub>eq</sub>–P–F<sub>eq</sub> bond angle of 134.3 (2)° are observed. Other bond lengths to phosphorus which display the expected differences between axial and equatorial coordination are P–F<sub>ax</sub> 1.602 (3), P–F<sub>eq</sub> 1.559 (3), P–N<sub>ax</sub> 1.742 (3) and P–N<sub>eq</sub> 1.621 (3) Å.

**Einleitung.** Durch Sublimierung wurden Kristalle der Verbindung in Form von farblosen Pyramiden erhalten, die bei 83–85° schmelzen und stark hygroskopisch sind. Für die Röntgenstrukturuntersuchung wurde daher ein Kristall mit den Abmessungen 0,18 × 0,20 × 0,16 mm in eine dünnwandige Glaskapillare eingeschmolzen. Die Gitterkonstanten wurden diffraktometrisch von 15 Reflexen mit höherem  $2\theta$ -Wert unter Verwendung von Mo  $K\alpha_1$  Strahlung ( $\lambda = 0,70926$  Å) bestimmt. Die Intensitätsdaten wurden auf einem

Syntex-Vierkreisdiffraktometer (Typ P2<sub>1</sub>) mit Mo  $K\alpha$  Strahlung (Graphit-Kristallmonochromator) im  $\theta$ – $2\theta$  ( $3,0 < 2\theta < 50,0^\circ$ ) Betrieb gesammelt. Die Scan-Geschwindigkeit variierte in linearer Weise zwischen 2,93° min<sup>-1</sup> (150 Impulse/Sekunde und weniger) und 29,30° min<sup>-1</sup> (3500 Impulse/Sekunde und mehr), wobei die Messzeiten für Untergrund und Reflex gleich waren. Von einer Gesamtzahl von 1377 beobachteten Reflexen wurden 240 (17,4%) nicht verwendet, weil  $I \leq 1,96\sigma(I)$  war ( $\sigma(I) = [I_{pk} + I_{bg}]^{1/2}$ , wobei  $I = I_{pk} - I_{bg}$ ). Die Daten wurden für Lorentz- und Polarisationsfaktoren, nicht aber für Absorptionseffekte ( $\mu(\text{Mo } K\alpha) = 14,3$  cm<sup>-1</sup>) korrigiert. Nach der Datenreduktion resultierten 1042 symmetrieunabhängige Reflexe.

Von der typisch zentrosymmetrischen Verteilung der normalisierten Struktur Faktoren ( $E$ -Werte) war die Raumgruppe  $P\bar{1}$  für diese Verbindung, die triklinen Symmetrie zeigt, anzunehmen. Diese Interpretation wurde durch die nachträgliche erfolgreiche Verfeinerung der Struktur bestätigt. Die Lagen des Phosphoratoms und der drei Chloratome konnten aus einer Patterson-Synthese direkt entnommen werden, die der