

Structure of 11,12-Dichloro-9,10-ethano-9,10-dihydro-1-anthroic Acid Methyl Ester, C₁₈H₁₄Cl₂O₂

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Abstract. $M_r = 333.2$, triclinic, $P\bar{1}$, $a = 9.782$ (2), $b = 13.269$ (7), $c = 12.942$ (9) Å, $\alpha = 88.77$ (7), $\beta = 97.67$ (7), $\gamma = 110.17$ (7)°, $V = 1562$ (2) Å³, $Z = 4$, $D_x = 1.42$ g cm⁻³, Mo $K\alpha$ radiation (graphite-crystal monochromator, $\lambda = 0.71069$ Å), $\mu(\text{Mo } K\alpha) = 4.15$ cm⁻¹, $F(000) = 688$, room temperature. Final conventional R factor = 0.042 ($R_w = 0.044$) for 2803 unique reflections and 355 parameters. The configuration at the Cl-substituted C atoms is *trans* with the Cl at the C atom closest to the methoxycarbonyl group pointing away from this group.

Introduction. The preparation of two isomers of the title compound in which the Cl atoms are *cis* has been previously described (Wang & Grubbs, 1977). As part of a study to probe charge distributions in base-induced 1,2 eliminations of HCl from the anions of the title compound and isomeric compounds (Grubbs *et al.*, 1983), the crystal structure determination was undertaken to provide definite proof of the stereochemistry of one particular isomer of the title compound.

Experimental. Crystal fragment $\sim 0.3 \times 0.4 \times 0.4$ mm cut from a larger colourless crystal, automated $P\bar{1}$ diffractometer, Mo $K\alpha$ radiation monochromatized with a graphite-crystal monochromator, unit-cell dimensions calculated by least-squares adjustment to the centred setting angles of 22 carefully selected reflections with $40 < 2\theta < 41^\circ$. Intensity data of 6748 reflections (the full sphere with $3^\circ < 2\theta < 42^\circ$) collected at a fixed scan rate of 4° min^{-1} , ω - 2θ scan technique, scan ranges calculated to start 0.7° below 2θ for $K\alpha_1$ ($\lambda = 0.70926$ Å) and to end 0.7° above 2θ for $K\alpha_2$ ($\lambda = 0.71354$ Å); backgrounds measured at the beginning and end of each scan. Two standard reflections monitored every 100 reflections showed no significant variation. Friedel-equivalent reflections averaged (R_{av} based on intensities: 0.030) to give 3374 unique reflections, 2803 of which had $I > 3\sigma(I)$ where $\sigma(I)$ is based on counting statistics. Lorentz and polarization corrections but not absorption. Direct methods [*MULTAN78* (Main, Hull, Lessinger, Ger-

main, Declercq & Woolfson, 1978) and *DIRDIF* (Beurskens *et al.*, 1981)]. The most probable *MULTAN* solution showed fragments of both independent molecules with the Cl atoms as the highest peaks. The top two *MULTAN* peaks were used as input to *DIRDIF* as Cl atoms. In a default run, *DIRDIF* gave all remaining 42 atoms among the top 44 peaks. Upon isotropic least-squares refinement [*SHELX* (Sheldrick, 1976)] the parameters converged with $R = 0.136$. Additional refinement with all atoms treated anisotropically, constrained idealized six-membered rings and calculated H-atom positions with fixed parameters ($U = 0.06$ Å²) converged at $R = 0.042$ and $R_w = 0.044$, using the 2803 'observed' reflections for 355 refined parameters. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = \sigma_c^2 + 0.0001F_o^2$ with σ_c^2 from counting statistics. $(\Delta/\sigma)_{max}$ in the last least-squares cycle (full matrix) < 0.8 , final $\Delta\rho$ excursions < 0.2 e Å⁻³.

Discussion. Final positional and thermal parameters are given in Table 1.† Molecular-geometry data are collected in Table 2. A stereoview showing the molecular conformation and packing is given in Fig. 1. Fig. 2 shows the crystallographic atomic numbering scheme.

Fig. 1 clearly shows the *trans* configuration of the Cl atoms at the $-\text{CHCl}-\text{CHCl}-$ bridge with Cl(1) pointing away from the methoxycarbonyl group. Bond distances and angles in the two independent molecules agree without significant differences. Although the conformation of both independent molecules is in general similar, there is a significant difference in the conformation of the methoxycarbonyl group (see Table 2). In molecule 2 the group is more rotated around the C(2)–C(3) bond by about 25° . There are no intermolecular contacts that are significantly shorter than the sum of the corresponding van der Waals radii.

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38846 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^2$) of non-hydrogen atoms

E.s.d.'s in parentheses. U_{eq} as defined by Hamilton (1959). For each atom, the top line refers to molecule 1, the bottom line to molecule 2.

	x	y	z	U_{eq}
Cl(1)	0.0748 (1)	0.43664 (9)	0.29022 (9)	7.69 (5)
	-0.0551 (1)	-0.1325 (1)	0.36127 (9)	8.73 (6)
Cl(2)	0.2700 (1)	0.23950 (8)	0.38992 (7)	6.17 (4)
	0.0726 (1)	0.06735 (9)	0.14020 (8)	7.64 (5)
O(1)	0.3449 (3)	0.2519 (2)	-0.1194 (2)	6.39 (12)
	0.7156 (3)	0.0411 (2)	0.3826 (2)	7.45 (13)
O(2)	0.4231 (3)	0.2157 (2)	0.0417 (2)	7.13 (14)
	0.5692 (3)	0.1203 (2)	0.2991 (2)	7.48 (13)
C(1)	0.3876 (6)	0.1685 (4)	-0.1594 (3)	7.42 (21)
	0.8414 (5)	0.1362 (4)	0.3741 (3)	8.25 (22)
C(2)	0.3725 (4)	0.2698 (3)	-0.0158 (3)	4.59 (15)
	0.5844 (4)	0.0432 (3)	0.3411 (3)	4.81 (17)
C(3)	0.3387 (2)	0.3661 (2)	0.0151 (1)	4.04 (14)
	0.4650 (2)	-0.0603 (2)	0.3547 (2)	4.33 (15)
C(4)	0.3017 (2)	0.4296 (2)	-0.0634 (1)	4.74 (15)
	0.4925 (2)	-0.1295 (2)	0.4307 (2)	5.56 (18)
C(5)	0.2816 (2)	0.5246 (2)	-0.0374 (1)	5.45 (17)
	0.3842 (2)	-0.2281 (2)	0.4439 (2)	6.46 (21)
C(6)	0.2986 (2)	0.5561 (2)	0.0670 (1)	5.08 (16)
	0.2484 (2)	-0.2575 (2)	0.3812 (2)	5.98 (18)
C(7)	0.3355 (2)	0.4927 (2)	0.1455 (1)	4.28 (15)
	0.2209 (2)	-0.1882 (2)	0.3051 (2)	4.99 (16)
C(8)	0.3556 (2)	0.3977 (2)	0.1195 (1)	3.88 (14)
	0.3292 (2)	-0.0896 (2)	0.2919 (2)	4.18 (15)
C(9)	0.3898 (4)	0.3385 (3)	0.2171 (2)	4.22 (14)
	0.2799 (4)	-0.0267 (3)	0.2037 (2)	4.57 (14)
C(10)	0.2583 (4)	0.3213 (3)	0.2787 (2)	4.56 (14)
	0.1393 (4)	-0.0129 (3)	0.2335 (3)	5.34 (16)
C(11)	0.2577 (4)	0.4315 (3)	0.3154 (3)	4.94 (15)
	0.0184 (4)	-0.1239 (3)	0.2397 (3)	5.68 (17)
C(12)	0.3656 (4)	0.5213 (3)	0.2597 (3)	4.49 (15)
	0.0831 (4)	-0.2123 (3)	0.2284 (3)	5.59 (16)
C(13)	0.5128 (3)	0.5143 (1)	0.3017 (2)	4.27 (15)
	0.1283 (3)	-0.1986 (2)	0.1199 (2)	5.32 (17)
C(14)	0.6294 (3)	0.5932 (1)	0.3599 (2)	5.09 (16)
	0.0796 (3)	-0.2735 (2)	0.0371 (2)	6.80 (19)
C(15)	0.7583 (3)	0.5734 (1)	0.3962 (2)	5.69 (17)
	0.1391 (3)	-0.2490 (2)	-0.0563 (2)	7.67 (24)
C(16)	0.7707 (3)	0.4747 (1)	0.3742 (2)	5.62 (17)
	0.2473 (3)	-0.1497 (2)	-0.0669 (2)	8.01 (24)
C(17)	0.6541 (3)	0.3957 (1)	0.3161 (2)	4.85 (16)
	0.2960 (3)	-0.0748 (2)	0.0159 (2)	6.28 (18)
C(18)	0.5251 (3)	0.4155 (1)	0.2798 (2)	4.17 (15)
	0.2365 (3)	-0.0992 (2)	0.1093 (2)	4.96 (16)

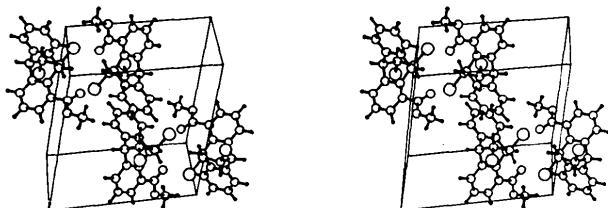


Fig. 1. Stereopair showing the molecular conformation and packing in minimum-overlap view.

Table 2. Molecular geometry [selected bond distances (\AA), torsional angles ($^\circ$) and bond angles ($^\circ$)]

Six-membered rings have fixed bond lengths of 1.395 \AA and angles of 120 $^\circ$. C—H distances are fixed at 1.08 \AA .

	Molecule 1	Molecule 2
Cl(1)—C(11)	1.799 (3)	1.800 (4)
Cl(2)—C(10)	1.800 (3)	1.798 (4)
O(1)—C(2)	1.342 (4)	1.333 (4)
O(2)—C(2)	1.199 (4)	1.194 (4)
O(1)—C(1)	1.438 (4)	1.441 (5)
C(7)—C(12)	1.499 (4)	1.504 (4)
C(9)—C(10)	1.551 (5)	1.547 (5)
C(10)—C(11)	1.549 (5)	1.546 (5)
C(12)—C(13)	1.502 (4)	1.517 (5)
C(2)—C(3)	1.501 (4)	1.490 (5)
C(8)—C(9)	1.532 (4)	1.524 (4)
C(9)—C(18)	1.507 (4)	1.494 (4)
C(11)—C(12)	1.534 (5)	1.530 (5)
C(18)—C(13)—C(12)—C(11)	60.8 (3)	62.5 (3)
C(13)—C(18)—C(9)—C(10)	-57.8 (3)	-55.5 (4)
C(9)—C(10)—C(11)—C(12)	12.0 (4)	7.4 (4)
C(12)—C(11)—C(10)—Cl(2)	133.6 (3)	129.7 (3)
C(9)—C(10)—C(11)—Cl(1)	134.5 (3)	129.7 (3)
Cl(1)—C(11)—C(10)—Cl(2)	-103.9 (3)	-108.0 (3)
C(7)—C(12)—C(11)—Cl(1)	-73.2 (4)	-70.0 (3)
C(18)—C(9)—C(10)—Cl(2)	-73.0 (3)	-70.9 (3)
C(8)—C(3)—C(2)—O(2)	-4.5 (5)	20.3 (5)
C(8)—C(3)—C(2)—O(1)	178.2 (3)	-159.8 (3)
C(3)—C(2)—O(1)—C(1)	173.6 (3)	179.4 (3)
C(1)—O(1)—C(2)	116.7 (3)	117.4 (3)
O(2)—C(2)—O(1)	122.1 (3)	122.3 (4)
C(3)—C(2)—O(1)	111.7 (3)	111.6 (3)
C(3)—C(2)—O(2)	126.2 (3)	126.1 (3)
C(12)—C(7)—C(6)	124.9 (1)	125.5 (2)
C(12)—C(7)—C(8)	115.0 (1)	114.4 (2)
C(9)—C(8)—C(7)	111.5 (1)	112.3 (2)
C(9)—C(8)—C(3)	128.5 (1)	127.7 (2)
C(4)—C(3)—C(2)	118.5 (2)	118.5 (2)
C(8)—C(3)—C(2)	121.3 (2)	121.5 (2)
C(10)—C(9)—C(8)	104.5 (2)	105.2 (3)
C(18)—C(9)—C(8)	106.6 (2)	105.7 (2)
C(18)—C(9)—C(10)	108.0 (2)	107.8 (2)
C(9)—C(10)—Cl(2)	140.6 (2)	110.8 (2)
C(11)—C(10)—Cl(2)	109.6 (2)	109.6 (2)
C(11)—C(10)—C(9)	109.6 (3)	110.3 (3)
C(10)—C(11)—Cl(1)	110.2 (2)	109.7 (2)
C(12)—C(11)—Cl(1)	111.2 (2)	111.3 (3)
C(12)—C(11)—C(10)	109.3 (3)	109.3 (3)
C(11)—C(12)—C(7)	108.0 (3)	108.4 (3)
C(13)—C(12)—C(7)	107.5 (3)	107.5 (3)
C(13)—C(12)—C(11)	103.5 (2)	104.3 (3)
C(17)—C(18)—C(9)	126.3 (1)	125.2 (2)
C(13)—C(18)—C(9)	113.7 (1)	114.8 (2)
C(14)—C(13)—C(12)	126.8 (1)	127.7 (2)
C(18)—C(13)—C(12)	113.2 (1)	112.2 (2)

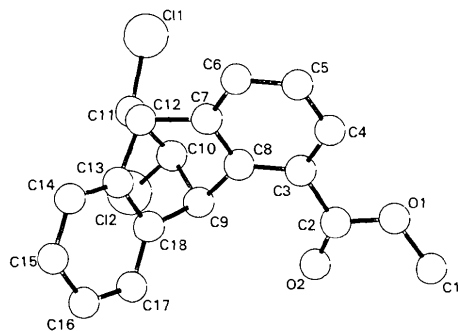


Fig. 2. Atomic numbering scheme for one molecule. In Table 1 the bottom line for each atom refers to the second (independent) molecule.

References

- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., GOULD, R. O., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G. & PARTHASARATHI, V. (1981). *DIRDIF81*. Tech. Rep. 1981/2. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- GRUBBS, E. J., SCHMIDT, S. P., WANG, C. T., GOODROW, M. H., LEWIS, R. M., DEARDURFF, L. A. & COFFEY, D. (1983). *J. Am. Chem. Soc.* To be published.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
- WANG, C. T. & GRUBBS, E. J. (1977). *J. Org. Chem.* **42**, 534.

Acta Cryst. (1984). **C40**, 125–127

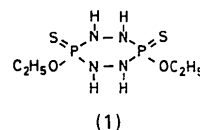
cis-3,6-Diethoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid, C₄H₁₄N₄O₂P₂S₂

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Abstract. $M_r = 276.238$, tetragonal, $P4_2/n$, $a = 11.506$ (2), $c = 9.278$ (1) Å, $V = 1228.3$ (6) Å³, $Z = 4$, $D_x = 1.494$ g cm⁻³, Ni-filtered Cu $K\alpha$, $\lambda = 1.54179$ Å, $\mu = 61.5$ cm⁻¹, $F(000) = 576$, $T = 293$ K, $R = 0.044$ for 1014 contributing reflections. The saturated six-membered inorganic heterocycle has an almost ideal twist conformation with interplanar angles around ring bonds of +63.5 (3) (PNNP), -32.1 (3) and -28.7 (3)° (NPN). The PNN bond angles range from 116.4 (3) to 118.5 (3)°, the NPN angle is 102.6 (2)°. Mean bond distances: P–N 1.643 (4), N–N 1.409 (5), P–S 1.925 (2), P–O 1.579 (3), O–C 1.470 (6) Å.



Einleitung. Schon mehrfach wurde an dieser Stelle über Strukturuntersuchungen an Phosphor-Hydrazin-Heterocyclen aus unserer Arbeitsgruppe berichtet (z.B. Engelhardt & Viertel, 1982). Sie dienen der Antwort auf die Fragestellung, welchen Einfluss unterschiedliche Substituenten auf die Ringkonformation haben.

Von Jürgens (1979) wurde erstmals ein Weg aufgezeigt, die *cis*- und *trans*-Isomeren der Titelverbindung (1) darzustellen. Es ist uns jetzt gelungen, für die Röntgenstrukturanalyse geeignete Einkristalle durch fraktionierte Kristallisation aus absolutem Ethanol zu gewinnen. Da sich bei der Untersuchung der analogen Methoxy- und Phenoxy-Verbindungen (Engelhardt & Jürgens, 1980; Engelhardt & Hartl, 1975, 1976) gezeigt hatte, dass die *trans*-Isomeren jeweils in Sesselform vorliegen, ist anzunehmen, dass auch das *trans*-Isomere von (1) Sesselform besitzt. Deshalb wurde von uns vorrangig das *cis*-Isomere untersucht, von dem eine Strukturvoraussage nicht ohne weiteres möglich war.

Experimentelles. Raumgruppe und ungefähre Gitterkonstanten wurden aus Drehkristall-, Weissenberg- und Präzessionsaufnahmen bestimmt. Reflexintensitäten und genaue Gitterkonstanten wurden auf einem DEC PDP 15/40 gesteuerten Stoe-Vierkreis-Diffraktometer vermessen; θ von 2,5 bis 64,5°, + h , + k , + l ; 1146 kristallographisch unabhängige Reflexe vermessen; zwei Standardreferenzreflexe nach je 80 Reflexen; Kristall: nadelförmig, *ca.* 0,07 × 0,07 × 0,45 mm, Kristallvolumen 0,0023 mm³; Absorptionskorrektur mit 6 Begrenzungsflächen (Programm *ABSCOR* im Programmsystem *XRAY 76*; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); Transmissionsfaktor 0,68 > A > 0,49 (Reflexe 13,0,1 bzw. 0,0,10). 225 Reflexe mit $I < 2\sigma(I)$ [$\sigma(I)$ = statistischer Fehler der Gesamtzählrate + 0,03I] wurden als unbeobachtet eingestuft und bei der Verfeinerung [Minimalisierung von $\sum w(|F_o| - |F_c|)^2$] nur berücksichtigt, wenn die berechnete Intensität grösser war als die beobachtete. Die Struktur wurde mit direkten Methoden gelöst (Programm *MULTAN*, Germain, Main & Woolfson, 1971). Nach zuerst isotroper, dann anisotroper Verfeinerung und anschließender Differenz-Fourier-Synthese ergaben sich die Positionen aller Atome. Die abschliessende Verfeinerung (H-Atome nicht mehr verfeinert) mit isotropem Extinktionsfaktor g (Larson, 1967) und Einführung einer Gewichtung [$w = K/(1,1 - 5 \times 10^{-2}F_o + 8 \times 10^{-3} \times$