

(Williams & Wallwork, 1967); in the latter it was interpreted as a specific interaction between the C=C group of TCNE and the 1,4 position in naphthalene.

The distance of 3.32 Å between the molecular planes is similar to that reported for the pyrene-TCNE complex (Ikemoto & Kuroda, 1968). The 18 000 cm⁻¹ band observed for skatole-TCNE is close to the 20 000 cm⁻¹ band observed for pyrene-TCNE corresponding to the electron transfer from the second highest orbital of pyrene to the lowest vacant orbital of TCNE.

A decomposition mechanism (Foster & Hanson, 1965) was suggested for the indole-TCNE complex *via* a complex to 3-tricyanovinylindole. We conclude that the C atom at the 3-substituted position in the skatole molecule plays a decisive role in stabilizing the charge-transfer crystal. This is consistent with the observation (Bruzzzone & Roselli, 1980) that indole-TCNE and 2-methylindole-TCNE do not form crystals.

We thank the CICPBA and the CONICET for financial support, the UNLP for use of the IBM 360/50

computer of the CESPI, and the Departamento de Física, Campus de São Carlos, Universidade de São Paulo, Brazil, for use of the Nonius CAD-4 diffractometer.

References

- BRUZZONE, L. & ROSELLI, M. E. (1980). *An. Asoc. Quim. Argent.* In the press.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
 FOSTER, R. & HANSON, P. (1965). *Tetrahedron*, **21**, 255.
 HANSON, A. W. (1964). *Acta Cryst.* **17**, 559-568.
 IKEMOTO, I. & KURODA, H. (1967). *Bull. Chem. Soc. Jpn.* **40**, 2009.
 IKEMOTO, I. & KURODA, H. (1968). *Acta Cryst.* **B24**, 383-387.
 SHELDRIK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **22**, 899-906.

Acta Cryst. (1980). **B36**, 1728-1731

The Structure of Methyl 6-(Diphenylphosphinyl)-3,4-dimethyl-3-cyclohexene-1-carboxylate

BY M. L. GŁÓWKA AND Z. GALDECKI

Institute of General Chemistry, Technical University of Łódź, 36 Żwirki, 90-924 Łódź, Poland

(Received 17 October 1979; accepted 24 March 1980)

Abstract. C₂₂H₂₅O₃P, *M_r* = 368.42, monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 14.235 (3), *b* = 12.768 (2), *c* = 11.062 (2) Å, β = 90.48 (2)°, *V* = 2010.5 Å³, *D_o* = 1.222 (by flotation), *D_c* = 1.217 Mg m⁻³, *F*(000) = 782. The structure was solved with *MULTAN* and refined by full-matrix least squares to a final *R* of 0.048 (*R_w* = 0.063) for 2027 intensities collected on a four-circle diffractometer with Cu radiation. The cyclohexene ring is in a slightly distorted half-chair conformation with asymmetry parameters Δ*C*₂ = 4.2 (5), Δ*C*₃ = 17.8 (5), φ̄ = 30.0 (5)°. The carboxyl group is *trans* to the diphenylphosphinyl group with a P-C-C-COOCH₃ torsional angle of 59.8 (6)°.

Introduction. The title compound is a model for studying the mechanism of the stereospecific synthesis of the optically active 17-phosphasteroid system used by Dr Bodalski and his group at the Institute of Organic Chemistry, Technical University of Łódź.

Also, the present study forms part of our X-ray investigation of the structures and conformations of phosphine oxides (Galdecki & Główka, 1977*a,b*, 1978; Główka, 1978; Galdecki, Główka, Bodalski & Pietrusiewicz, 1979).

Colourless crystals of the compound were kindly supplied by Dr J. Koszuk. Intensities from a spherical crystal (about 0.3 mm in diameter) were recorded on a Syntex diffractometer with graphite-monochromated Cu *K*α radiation. From 2027 collected reflections, 1896 had |*F*| ≥ 3σ(*F*). The intensities were not corrected for absorption (*μ**r* = 2.0).

The calculations were performed using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on a RIAD 32 computer, and *MULTAN* (Germain, Main & Woolfson, 1971) on an ODRA 1305 machine. The weighting scheme applied in the refinement of the structure was *w*⁻¹ = [σ(*F_o*)]². Neutral-atom scattering factors given by Doyle & Turner (1968) for P, O and C

and those in *International Tables for X-ray Crystallography* (1962) for H were employed.

The structure of the compound was solved using *MULTAN*. The best solution characterized by a *RESID* of 35.6 and a *COMFOM* of 2.1 gave an *E* map based on $400 E \geq 1.3$ which enabled us to locate ten of the 26 non-hydrogen atoms. The subsequent Fourier synthesis revealed all the remaining heavy atoms. The structure was refined by full-matrix (isotropic) and block-diagonal least squares. During the anisotropic refinement the matrix was divided into two blocks only, each holding positional and anisotropic temperature parameters for over half the heavy atoms. The H atoms were found from a difference map and refined with isotropic temperature factors. Finally, four cycles of block-diagonal refinement, with each block holding positional and temperature parameters for one atom, resulted in an *R* of 0.048 ($R_w = 0.063$).

Discussion. Fig. 1 is a projection of the molecule showing the atom-numbering scheme. Tables 1 and 2 give the final parameters and the C—H bond lengths. The molecules of the compound are well separated in the crystal. There are no intermolecular contacts short enough to affect the conformation of the molecule. The shortest intermolecular distances between non-hydrogen atoms are 3.23 (1), 3.28 (1) and 3.45 (1) Å for O(2)···O(3), O(1)···C(2) and O(1)···C(16), respectively (the first atom is at x, y, z and the second at $x, 1.5 - y, 0.5 + z$). The bond lengths (Table 3) and angles (Table 4) agree well with values in the literature. As is usual in phosphine oxides, distortion of the P coor-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35137 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

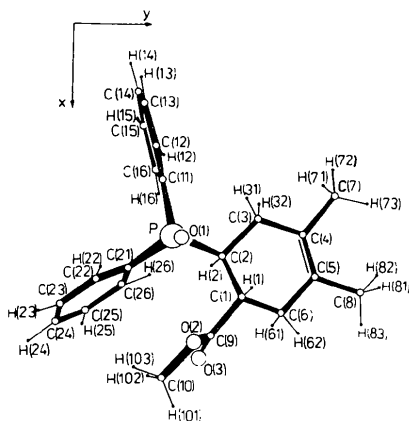


Fig. 1. Molecule of methyl 6-(diphenylphosphinyl)-3,4-dimethyl-3-cyclohexene-1-carboxylate and the numbering system used in the paper.

Table 1. *Non-hydrogen atom coordinates* ($\times 10^4$) *with their e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	B_{150} (Å ²)
P	6966 (1)	7106 (1)	6439 (1)	2.3 (1)
O(1)	6968 (1)	7269 (1)	7767 (1)	3.4 (1)
O(2)	9215 (1)	7680 (2)	7424 (2)	4.0 (1)
O(3)	9538 (1)	7771 (2)	5470 (2)	4.7 (2)
C(1)	8236 (2)	8761 (2)	6239 (2)	2.6 (2)
C(2)	7363 (2)	8260 (2)	5623 (2)	2.3 (2)
C(3)	6566 (2)	9066 (2)	5593 (3)	3.6 (2)
C(4)	6859 (2)	10160 (2)	5255 (3)	3.3 (2)
C(5)	7749 (2)	10466 (2)	5233 (2)	3.2 (2)
C(6)	8538 (2)	9735 (2)	5548 (3)	3.7 (2)
C(7)	6051 (2)	10876 (3)	4930 (4)	5.9 (3)
C(8)	8055 (2)	11561 (3)	4887 (3)	5.9 (3)
C(9)	9054 (2)	8027 (2)	6314 (2)	3.0 (2)
C(10)	9964 (2)	6921 (3)	7561 (3)	4.2 (2)
C(11)	5805 (2)	6770 (2)	5897 (2)	2.7 (2)
C(12)	5112 (2)	6612 (2)	6762 (3)	3.7 (2)
C(13)	4216 (2)	6305 (2)	6406 (3)	5.0 (3)
C(14)	4012 (2)	6148 (2)	5200 (3)	5.1 (3)
C(15)	4689 (2)	6303 (2)	4339 (3)	4.2 (2)
C(16)	5590 (2)	6616 (2)	4683 (2)	3.5 (2)
C(21)	7705 (2)	6026 (2)	6004 (2)	2.6 (2)
C(22)	7934 (2)	5289 (2)	6870 (3)	3.8 (2)
C(23)	8490 (2)	4447 (2)	6574 (3)	5.1 (3)
C(24)	8842 (2)	4335 (2)	5423 (3)	5.0 (2)
C(25)	8612 (2)	5053 (2)	4566 (3)	4.4 (2)
C(26)	8046 (2)	5907 (2)	4838 (2)	3.5 (2)

Table 2. *Hydrogen atom parameters* (*positional* $\times 10^3$) *and C—H distances*

The numbers of the H atoms refers to those C atoms to which they are bonded.

	<i>x</i>	<i>y</i>	<i>z</i>	$10B_{150}$ (Å ²)	C—H (Å)
H(1)	805 (1)	894 (2)	705 (2)	12 (5)	0.97 (2)
H(2)	754 (2)	806 (2)	481 (2)	10 (5)	0.97 (2)
H(12)	531 (2)	666 (2)	762 (2)	36 (8)	1.00 (3)
H(13)	368 (2)	622 (2)	702 (2)	39 (8)	1.04 (3)
H(14)	344 (2)	591 (3)	501 (3)	56 (9)	0.89 (3)
H(15)	455 (2)	618 (2)	347 (2)	32 (7)	0.99 (3)
H(16)	611 (2)	673 (2)	408 (2)	34 (7)	1.01 (3)
H(22)	770 (2)	540 (2)	770 (2)	41 (7)	0.99 (3)
H(23)	867 (2)	395 (2)	723 (3)	55 (8)	0.99 (3)
H(24)	921 (2)	370 (3)	521 (3)	70 (11)	0.99 (4)
H(25)	888 (2)	497 (3)	377 (3)	61 (10)	0.97 (3)
H(26)	782 (3)	651 (3)	424 (3)	76 (11)	1.07 (4)
H(31)	624 (2)	907 (2)	646 (2)	36 (8)	1.07 (3)
H(32)	613 (2)	882 (2)	502 (2)	28 (7)	0.94 (3)
H(61)	897 (2)	1017 (2)	605 (2)	29 (7)	1.00 (3)
H(62)	885 (3)	947 (3)	472 (3)	73 (11)	1.08 (4)
H(71)	618 (3)	1158 (3)	499 (3)	75 (11)	0.92 (4)
H(72)	582 (2)	1058 (3)	410 (3)	81 (10)	1.05 (4)
H(73)	549 (2)	1079 (3)	559 (3)	80 (11)	1.10 (4)
H(81)	807 (3)	1195 (3)	553 (4)	111 (13)	0.86 (4)
H(82)	769 (3)	1191 (3)	420 (3)	75 (11)	1.02 (4)
H(83)	873 (3)	1158 (3)	455 (3)	70 (10)	1.03 (4)
H(101)	1052 (2)	716 (3)	730 (3)	59 (10)	0.90 (3)
H(102)	991 (3)	679 (3)	839 (3)	75 (10)	0.94 (3)
H(103)	977 (3)	627 (3)	716 (3)	72 (11)	0.98 (4)

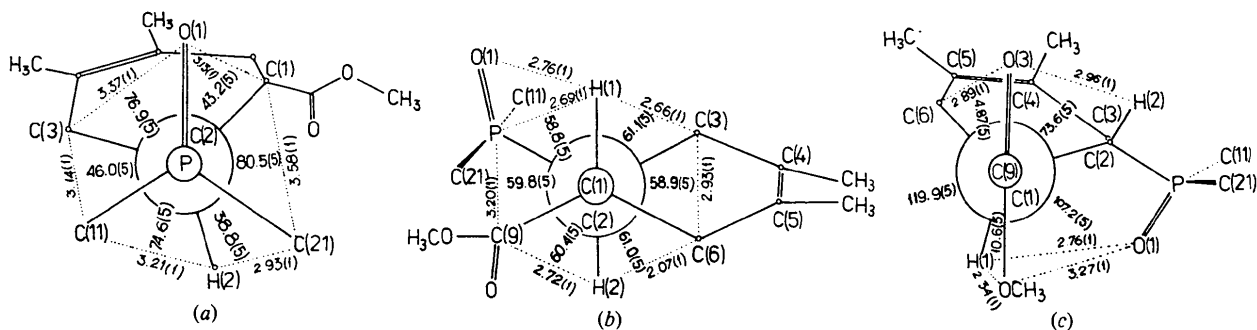


Fig. 2. Newman projections down (a) P—C(2), (b) C(1)—C(2) and (c) C(9)—C(1), showing some interatomic distances (Å) and torsion angles (°).

dination tetrahedron is observed, *i.e.* O=P—C angles increase to a mean value of 112° while C—P—C angles decrease to 105–108°. Both phenyl rings have considerable freedom of movement and temperature factors of the ring atoms are about 1.5 times the values

Table 3. Bond lengths (Å)

P—O(1)	1.483 (2)	C(8)—C(5)	1.515 (4)
P—C(2)	1.821 (3)	C(9)—C(1)	1.496 (4)
P—C(11)	1.805 (3)	C(11)—C(12)	1.396 (4)
P—C(21)	1.803 (3)	C(12)—C(13)	1.388 (4)
O(2)—C(9)	1.323 (3)	C(13)—C(14)	1.377 (5)
O(2)—C(10)	1.448 (4)	C(14)—C(15)	1.375 (4)
O(3)—C(9)	1.210 (3)	C(15)—C(16)	1.394 (4)
C(1)—C(2)	1.551 (3)	C(16)—C(11)	1.389 (4)
C(2)—C(3)	1.532 (4)	C(21)—C(22)	1.380 (4)
C(3)—C(4)	1.506 (4)	C(22)—C(23)	1.376 (4)
C(4)—C(5)	1.326 (4)	C(23)—C(24)	1.380 (5)
C(5)—C(6)	1.499 (4)	C(24)—C(25)	1.356 (4)
C(6)—C(1)	1.523 (4)	C(25)—C(26)	1.391 (4)
C(7)—C(4)	1.510 (4)	C(26)—C(21)	1.390 (4)

Table 4. Bond angles (°)

O(1)—P—C(2)	112.3 (1)	C(1)—C(6)—C(5)	114.3 (2)
O(1)—P—C(11)	110.9 (1)	O(2)—C(9)—C(1)	113.0 (2)
O(1)—P—C(21)	112.0 (1)	O(2)—C(9)—O(3)	122.0 (3)
C(2)—P—C(11)	108.3 (1)	O(3)—C(9)—C(1)	125.0 (2)
C(2)—P—C(21)	107.6 (1)	P—C(11)—C(12)	117.2 (2)
C(11)—P—C(21)	105.3 (1)	P—C(11)—C(16)	123.3 (2)
C(9)—O(2)—C(10)	116.3 (2)	C(12)—C(11)—C(16)	119.4 (2)
C(2)—C(1)—C(6)	110.1 (2)	C(11)—C(12)—C(13)	120.0 (3)
C(2)—C(1)—C(9)	112.7 (2)	C(12)—C(13)—C(14)	120.1 (3)
C(6)—C(1)—C(9)	108.5 (2)	C(13)—C(14)—C(15)	120.5 (3)
P—C(2)—C(1)	111.5 (2)	C(14)—C(15)—C(16)	120.0 (3)
P—C(2)—C(3)	108.8 (2)	C(15)—C(16)—C(11)	120.0 (2)
C(1)—C(2)—C(3)	108.9 (2)	P—C(21)—C(22)	118.1 (2)
C(2)—C(3)—C(4)	114.9 (2)	P—C(21)—C(26)	122.7 (2)
C(3)—C(4)—C(5)	123.0 (2)	C(22)—C(21)—C(26)	119.2 (2)
C(3)—C(4)—C(7)	114.1 (2)	C(21)—C(22)—C(23)	120.1 (3)
C(5)—C(4)—C(7)	122.9 (2)	C(22)—C(23)—C(24)	120.9 (3)
C(4)—C(5)—C(6)	121.7 (2)	C(23)—C(24)—C(25)	119.2 (3)
C(4)—C(5)—C(8)	123.6 (3)	C(24)—C(25)—C(26)	121.0 (3)
C(6)—C(5)—C(8)	114.7 (2)	C(25)—C(26)—C(21)	119.6 (3)

found for the remaining atoms. Also the χ^2 test calculated for the rings shows that the sets of atoms are non-planar, within experimental error $|\sum d^2/\sigma^2|$ is 731 for C(21)—C(26) and 79 for C(11)—C(16), although no reason for such non-planarity can be seen.

The cyclohexene ring adopts a distorted half-chair conformation with a twofold axis bisecting the C(4)=C(5) double bond. Similar distortions have been observed in other *trans*-3,4-disubstituted cyclohexenes (Moron, 1967; Pedone, Benedetti, Immirzi & Allegra, 1970). The asymmetry parameters (Duax & Norton, 1975) for the cyclohexene ring are $\Delta C_2^{1,2} = 4.2 (5)$, $\Delta C_5^1 = 17.8 (5)$, $\bar{\phi} = 30.0 (5)^\circ$ in this structure, in comparison with 3.5, 19.6, 30.7° (Pedone *et al.*, 1970) and 6.5, 13.2, 27.3° (Moron, 1967) in similar compounds. The conformation of the molecule is shown in Fig. 2 by means of Newman projections viewed in the directions of the P—C(2), C(1)—C(2) and C(9)—C(1) bonds. Intramolecular interactions between the C(21)—C(26) phenyl ring and the carboxymethyl group force the conformation of the P—C(2) bond to be intermediate between staggered and eclipsed (Fig. 2a). Thus the planes defined by C(21)—C(26) and C(1), C(9), C(10), O(2), O(3) are nearly parallel (Fig. 1). The angle between the planes is only 19 (1)°.

The authors thank Drs R. Bodalski and J. Koszuk of the Institute of Organic Chemistry, Technical University of Łódź, for the crystals and for suggesting the problem, and Mr J. Perka for technical assistance. This research was supported by project MR.I.9 from the Polish Academy of Sciences.

References

- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390–397.
 DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, pp. 16–22. New York: Plenum.
 GALDECKI, Z. & GŁÓWKA, M. L. (1977a). *Acta Cryst.* B33, 2650–2653.
 GALDECKI, Z. & GŁÓWKA, M. L. (1977b). *Acta Cryst.* B33, 3908–3911.

- GALDECKI, Z. & GLÓWKA, M. L. (1978). *Acta Cryst.* B34, 2938–2940.
- GALDECKI, Z., GLÓWKA, M. L., BODALSKI, R. & PIETRUSIEWICZ, K. M. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1720–1722.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- GLÓWKA, M. L. (1978). *Acta Cryst.* B34, 3089–3901.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- MORNON, J. P. (1967). *Acta Cryst.* 23, 367–376.
- PEDONE, C., BENEDETTI, E., IMMIRZI, A. & ALLEGRA, G. (1970). *J. Am. Chem. Soc.* 92, 3549–3552.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1980). B36, 1731–1732

Structure de l'Azodiformaldéhyde-dioxime

PAR C. BOIS

Laboratoire de Recherches de Chimie Systématique, Université Pierre et Marie Curie, 8 rue Cuvier, 75005 Paris, France

ET J. ARMAND ET P. BASSINET

Laboratoire de Physicochimie des Solutions, LA CNRS 161, Université Pierre et Marie Curie, 75230 Paris CEDEX 05, France

(Reçu le 22 octobre 1979, accepté le 19 mars 1980)

Abstract. C₂H₄N₄O₂, monoclinic, $P2_1/c$, $a = 4.451$ (4), $b = 9.520$ (6), $c = 6.340$ (5) Å, $\beta = 115.76$ (6)°, $Z = 2$, $d_m = 1.59$ (1), $d_x = 1.59$ Mg m⁻³. The structure was solved by direct methods and refined to $R = 0.043$. The azo group has an *E* configuration (*trans*) and the oximino groups are both *E* (*syn-H*).

Introduction. Les azodialdéhyde-dioximes RC(NOH)N–NC(NOH)R' ont été peu étudiées (Meyer & Constam, 1882; Wieland, 1907; Armand, Bassinet & Souchay, 1970). Les spectres RMN et UV (Armand, Bassinet & Souchay, 1970) ont montré que les trois composés connus correspondant à $R = R' = H$ (1), $R = R' = CH_3$ (2), $R = H, R' = CH_3$ (3) avaient la même structure. Mais les configurations respectives du groupe azoïque et des groupes oximes n'avaient pas pu être déterminées. Cela nous a conduit à entreprendre l'étude structurale, aux rayons X, du composé (1).

Les intensités diffractées ont été mesurées à l'aide d'un diffractomètre quatre cercles Philips, jusqu'à un angle θ de 25° (radiation Mo K α , monochromateur de graphite, balayage $\omega-2\theta$). Seules 572 réflexions dont l'intensité satisfaisait à la relation $I \geq 4\sigma(I)$ ont été retenues pour la détermination structurale (699 réflexions mesurées).

Au cours des enregistrements, trois réflexions standard ont été testées pour vérifier que le cristal ne se décomposait pas. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation mais aucune

correction d'absorption n'a été nécessaire: l'échantillon utilisé était une bipyramide de dimensions assez régulières n'excédant pas 0,3 mm ($\mu = 0,15$ mm⁻¹).

L'existence de deux molécules dans une maille de groupe spatial $P2_1/c$ impliquait pour la molécule l'existence d'un centre de symétrie confondu avec un centre d'inversion de la maille.

L'application du programme *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) a permis de localiser les quatre atomes indépendants. L'affinement de tous les paramètres atomiques en supposant l'agitation thermique anisotrope a conduit à un indice résiduel de 0,056. Une série de Fourier différence a fait apparaître les deux atomes d'hydrogène; leurs coordonnées ont été affinées, mais on leur a attribué le facteur d'agitation thermique de l'atome porteur en fin d'affinement isotrope.

Le facteur de pondération adopté au cours des affinements était $w = 1/\sigma^2(F)$. Les valeurs finales des coefficients R et R_w sont respectivement 0,043 et 0,060.*

Le Tableau 1 rassemble les différents paramètres atomiques ainsi que leurs écarts types. Les principaux angles et distances sont donnés dans le Tableau 2.

* Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 35213; 6 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.