

upon the size of the starting set of phases, this is not so for the refinement of a given set of phase angles by electron density modification. In this case, significant improvement in phase angles can be accomplished at any resolution by performing a small number of cycles of inverse transform calculations of a suitably modified density. This could prove to be an expeditious way to additionally improve MIR 'best' electron density maps.

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Crystal Structures of Two Forms of 1,2-Bis(diphenylphosphino)ethane

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Abstract

Crystals of both forms of the title compound, C₂₆H₂₄P₂, are monoclinic (space group *P*₂₁/*n*) with unit-cell dimensions $a = 13.154$ (7), $b = 5.508$ (4), $c = 15.960$ (8) Å, $\beta = 110.75$ (6)°, $Z = 2$ for form (I) and

$a = 9.078$ (9), $b = 5.763$ (4), $c = 21.314$ (12) Å, $\beta = 100.78$ (4)°, $Z = 2$ for form (II). The structures were both solved from X-ray diffractometer data with direct methods for (I) and the heavy-atom technique for (II). Refinement by full-matrix least squares gave $R = 4.37\%$ for 1257 independent reflections and $R =$

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5.26% for 1545 independent reflections for (I) and (II) respectively. The structural data and the half-normal probability plot support the hypothesis that the conformations of the two compounds are practically identical and that the slight differences in the IR spectra are mainly due to different packing modes.

Introduction

It is well known that phosphines play an important role in coordination chemistry, mainly due to their reducing and π -acceptor properties, which permit the stabilization of low oxidation states in several transition-metal elements (Ugo, 1968; Karayannis, Mikulski & Pytlewski, 1971). An interesting example of the utilization of this kind of compound is shown by the molybdenum-phosphine complexes which are able to fix dinitrogen molecules (Allen, Harris, Loescher, Stevens & Whiteley, 1973; Shilov, 1974; Chatt, 1975).

In connection with a research program involving synthesis, structure and reactivity of organotin adducts with organophosphorus and organoarsenic derivatives (Nardelli, Pelizzi & Pelizzi, 1976, 1977, 1978; Pelizzi, Pelizzi & Tarasconi, 1977; Nardelli, Pelizzi, Pelizzi & Tarasconi, 1978), bis(diphenylphosphino)ethane (hereafter abbreviated to DIPHOS) has been taken into account as a ligand to tin. From the reaction of DIPHOS with nitratotriphenyltin in dry acetone, a dinuclear adduct of formula $[\text{SnPh}_3(\text{NO}_3)]_2[\text{OPPh}_2(\text{CH}_2)_2\text{Ph}_2\text{PO}]$ (Nardelli, Pelizzi & Pelizzi, 1979) has been isolated in which the phosphoric ligand has been oxidized to bis(diphenylphosphinoyl)ethane by the action of the covalent nitrate group. Besides this tin adduct, small amounts of a colorless crystalline product were obtained having the same molecular formula as the DIPHOS reagent, but exhibiting slight differences in the vibrational spectra. The aim of this paper is to compare these two crystalline forms of DIPHOS by X-ray structural analysis.

Experimental

As mentioned above, compound (I) was isolated as the unreacted product from the reaction solution of DIPHOS with SnPh_3NO_3 in anhydrous acetone and under nitrogen atmosphere, the main product being $[\text{SnPh}_3(\text{NO}_3)]_2[\text{OPPh}_2(\text{CH}_2)_2\text{Ph}_2\text{PO}]$. Compound (II) was obtained by slow evaporation, at room temperature, of an acetone solution of commercial bis(diphenylphosphino)ethane. Both compounds melt at 411–413 K without decomposition.

Preliminary cell dimensions and space-group information were deduced from rotation and Weissenberg photographs taken with $\text{Cu } K\alpha$ radiation. Both crystals were found to be monoclinic, with extinctions of $0k0, k$

$\neq 2n$, and $h0l, h + l \neq 2n$, uniquely defining the space group $P2_1/n$ [a non-standard orientation for the C_{2h}^5 space group (No. 14); its equivalent positions are: $x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$]. Accurate cell parameters were determined by a least-squares refinement of the setting angles for 20 reflections measured on an automatic single-crystal Siemens AED diffractometer. Most significant crystal data are as follows:

$\text{C}_{26}\text{H}_{24}\text{P}_2, M_r = 398.4$.

Compound (I): $a = 13.154$ (7), $b = 5.508$ (4), $c = 15.960$ (8) Å, $\beta = 110.75$ (6)°; $U = 1081.3$ Å³, $Z = 2$, $D_c = 1.22$ Mg m⁻³, $F(000) = 420$; Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo } K\alpha) = 0.17$ mm⁻¹.

Compound (II): $a = 9.078$ (9), $b = 5.763$ (4), $c = 21.314$ (12) Å, $\beta = 100.78$ (4)°; $U = 1095.4$ Å³, $Z = 2$, $D_c = 1.21$ Mg m⁻³, $F(000) = 420$; Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å; $\mu(\text{Cu } K\alpha) = 1.74$ mm⁻¹.

Intensity data were collected at room temperature by single-crystal diffractometry using the 'five points' technique (Hoppe, 1969) with Mo $K\alpha$ radiation ($5.0^\circ < 2\theta < 54.0^\circ$) for (I) and Cu $K\alpha$ radiation ($4.0^\circ < 2\theta < 130.0^\circ$) for (II); the scan speed was $2.0^\circ \text{ min}^{-1}$. The intensities of 2331 and 1886 independent reflections were measured for (I) and (II) respectively, and of these 1257 for (I) and 1545 for (II) with intensities $> 2[\sigma^2(I) + (0.005I)^2]^{1/2}$, where I is the relative intensity and $\sigma^2(I)$ its variance, were considered as observed and used in the analysis. A reference reflection for each compound was periodically measured during data collection to check crystal alignment and/or decomposition, and its intensity was found to show only statistical variations and no crystal decay. After corrections for Lorentz and polarization effects, the structure amplitudes were put on an absolute scale, first correlating the observed and calculated values and then refining the scale factor for the F_o as a variable parameter in the least-squares procedure.

The infrared spectra were registered on a Perkin-Elmer Model 457 spectrophotometer in the 4000–250 cm⁻¹ region with KBr disks.

Structure determination and refinement

The structure of (I) was solved by multisolution \sum_2 sign expansion with *SHELX 76* (Sheldrick, 1976). The E map obtained from the set having the highest reliability index (parachor) contained the whole structure with the exception of the hydrogen atoms. Refinement by full-matrix isotropic least squares gave $R = 0.1052$ and this value improved to 0.0713 after two anisotropic cycles. At this stage a difference Fourier map was valuable in locating all the hydrogen atoms. Further refinement of 175 variables over 1257 data, including isotropic thermal parameters for the hydrogen atoms, converged to $R = 0.0437$.

The solution of the structure of (II) was accomplished with the standard heavy-atom technique. The positional parameters of the phosphorus atom were deduced from a Patterson map and used to phase the

Table 1. Fractional atomic coordinates ($\times 10^4$ for P and C, $\times 10^3$ for H), with estimated standard deviations in parentheses

	x	y	z
Compound (I)			
P	5904 (1)	2134 (2)	9315 (1)
C(1)	4859 (2)	1734 (6)	8214 (2)
C(2)	4052 (3)	3433 (7)	7911 (3)
C(3)	3249 (4)	3198 (10)	7084 (3)
C(4)	3248 (3)	1299 (9)	6559 (3)
C(5)	4028 (3)	-429 (9)	6847 (2)
C(6)	4828 (3)	-217 (7)	7671 (2)
C(7)	7087 (2)	879 (7)	9133 (2)
C(8)	7497 (4)	2190 (10)	8595 (3)
C(9)	8418 (5)	1408 (15)	8457 (5)
C(10)	8942 (4)	-594 (15)	8837 (4)
C(11)	8555 (4)	-1902 (12)	9371 (4)
C(12)	7628 (3)	-1173 (9)	9520 (3)
C(13)	5528 (2)	-292 (7)	9931 (2)
H(1)	412 (3)	483 (9)	823 (3)
H(2)	275 (3)	421 (8)	692 (3)
H(3)	274 (3)	121 (7)	602 (3)
H(4)	395 (3)	-182 (8)	650 (3)
H(5)	535 (3)	-137 (8)	788 (3)
H(6)	711 (3)	380 (8)	828 (3)
H(7)	848 (4)	227 (9)	801 (4)
H(8)	958 (4)	-100 (8)	881 (3)
H(9)	879 (4)	-353 (8)	963 (3)
H(10)	735 (4)	-222 (8)	989 (3)
H(11)	606 (3)	-37 (6)	1046 (2)
H(12)	547 (2)	-184 (6)	964 (2)
Compound (II)			
P	3047 (1)	6930 (1)	4466 (0)
C(1)	3751 (3)	6891 (5)	3712 (1)
C(2)	4581 (4)	8778 (6)	3561 (2)
C(3)	5109 (4)	8812 (7)	2992 (2)
C(4)	4818 (4)	6993 (7)	2573 (2)
C(5)	4003 (4)	5115 (7)	2715 (2)
C(6)	3466 (3)	5070 (6)	3279 (1)
C(7)	1222 (3)	5565 (6)	4217 (1)
C(8)	150 (4)	6886 (8)	3807 (2)
C(9)	-1293 (5)	6048 (13)	3626 (2)
C(10)	-1718 (5)	3998 (13)	3837 (3)
C(11)	-670 (5)	2673 (10)	4247 (2)
C(12)	782 (4)	3457 (7)	4426 (2)
C(13)	4180 (3)	4623 (6)	4908 (1)
H(1)	470 (4)	1036 (7)	389 (2)
H(2)	592 (4)	1018 (6)	298 (2)
H(3)	538 (5)	711 (8)	217 (2)
H(4)	367 (4)	388 (7)	238 (2)
H(5)	277 (4)	382 (6)	334 (2)
H(6)	37 (4)	864 (7)	364 (2)
H(7)	-198 (7)	669 (10)	327 (3)
H(8)	-280 (6)	333 (9)	370 (2)
H(9)	-88 (5)	144 (9)	441 (2)
H(10)	147 (6)	269 (9)	476 (2)
H(11)	387 (4)	462 (7)	539 (2)
H(12)	411 (4)	311 (7)	462 (2)

initial structure factor calculation. A Fourier synthesis at this stage revealed the positions of all non-hydrogen atoms. Two cycles of full-matrix isotropic least-squares refinement, followed by two cycles of full-matrix anisotropic refinement, produced convergence of R to 0.0782. The contributions of the hydrogen atoms, directly located from the final difference Fourier map and refined isotropically, improved R to 0.0526 (175 variables over 1545 data).

For both compounds the quantity minimized was $\sum w(\Delta F)^2$, in which the weighting function was of the form $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$. All calculations were made on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna. Final atomic coordinates are given in Table 1.*

Results and discussion

The structure of (I) and (II) is depicted in Fig. 1. In both (I) and (II) the unit cell contains two molecules of formula $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, with the middle of the $C(sp^3)-C(sp^3)$ bond on a crystallographic center of symmetry. Bond lengths and angles are given in Tables 2 and 3, respectively, together with their estimated standard deviations. The agreement between corresponding values is fairly good, with none of them differing from the weighted mean, which is also given in the tables, at a significance level of 0.001. The three P-C bond lengths in each compound [average 1.822 Å in (I) and 1.829 Å in (II)] are similar within experimental error. It seems, therefore, that there is no

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34341 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

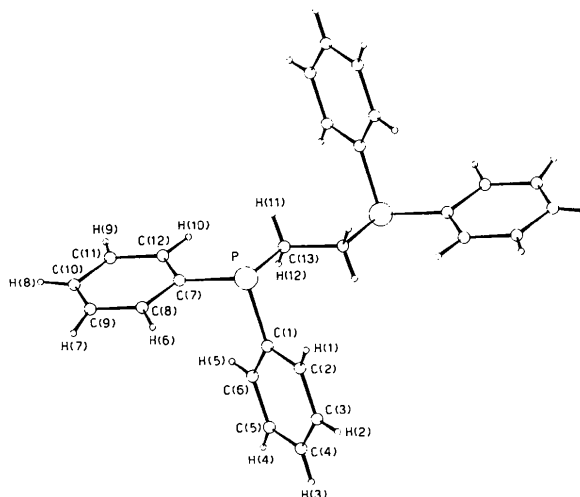


Fig. 1. Compounds (I) and (II). Projection of the structure.

evidence for a lengthening of this bond in going from $C(sp^2)$ to $C(sp^3)$, unlike most related compounds (Gaughan, Ziolo & Dori, 1971; Drew, 1972; Field, Wheatley & Bhaduri, 1974).

The presence of the lone pair on phosphorus justifies the values of the C–P–C angles which are all significantly less than the tetrahedral value of 109.5° , with the $C(sp^2)$ –P– $C(sp^3)$ angles slightly larger than the $C(sp^2)$ –P– $C(sp^2)$ angle. The P–C–C–P chain is constrained to the *trans* configuration by crystallographic requirements. The torsion angles, which are reported in Table 4, are practically identical in the two forms. The phenyl rings are perfectly planar in both compounds and nearly perpendicular to one another, the dihedral angle being $99.9(3)^\circ$ for (I) and $99.6(3)^\circ$ for (II). The phosphorus atom is practically coplanar with the C(1)–C(6) ring, while it is slightly displaced, probably for steric reasons, out of the C(7)–C(12) ring plane [0.08 Å for (I), 0.13 Å for (II)]. The C–C phenyl distances range from 1.328 to 1.382 Å in (I) and from 1.346 to 1.404 Å in (II), while the intra-ring C–C–C bond angles range from 117.6 to 122.1° in (I), and from 118.0 to 122.0° in (II).

On the basis of bond lengths, bond angles, torsion angles and dihedral angles, it can be argued that the differences, if any, existing between the two modifi-

Table 2. Bond lengths (Å) for the two compounds together with the weighted mean

	(I)	(II)	Weighted mean
P–C(1)	1.820 (3)	1.837 (5)	1.825 (7)
P–C(7)	1.818 (4)	1.821 (5)	1.819 (3)
P–C(13)	1.828 (4)	1.830 (5)	1.829 (3)
C(1)–C(2)	1.368 (5)	1.394 (5)	1.381 (13)
C(2)–C(3)	1.374 (6)	1.385 (7)	1.379 (7)
C(3)–C(4)	1.340 (7)	1.370 (6)	1.357 (15)
C(4)–C(5)	1.355 (6)	1.376 (6)	1.365 (11)
C(5)–C(6)	1.367 (4)	1.379 (6)	1.371 (6)
C(6)–C(1)	1.372 (5)	1.389 (4)	1.379 (9)
C(7)–C(8)	1.370 (7)	1.404 (6)	1.390 (17)
C(8)–C(9)	1.375 (10)	1.382 (7)	1.380 (7)
C(9)–C(10)	1.328 (11)	1.346 (10)	1.338 (12)
C(10)–C(11)	1.346 (10)	1.393 (8)	1.375 (24)
C(11)–C(12)	1.382 (8)	1.378 (6)	1.379 (5)
C(12)–C(7)	1.362 (6)	1.378 (5)	1.371 (9)
C(13)–C(13 ^b)	1.516 (4)	1.530 (5)	1.521 (7)
C(2)–H(1)	0.91 (5)	1.14 (4)	1.05 (11)
C(3)–H(2)	0.83 (4)	1.08 (4)	0.95 (13)
C(4)–H(3)	0.89 (3)	1.09 (5)	0.94 (9)
C(5)–H(4)	0.93 (4)	1.01 (4)	0.97 (5)
C(6)–H(5)	0.91 (4)	0.98 (3)	0.94 (5)
C(8)–H(6)	1.06 (4)	1.10 (4)	1.08 (4)
C(9)–H(7)	0.88 (6)	0.96 (5)	0.93 (5)
C(10)–H(8)	0.88 (5)	1.04 (5)	0.96 (9)
C(11)–H(9)	0.99 (5)	0.83 (5)	0.91 (9)
C(12)–H(10)	0.98 (5)	0.96 (5)	0.97 (4)
C(13)–H(11)	0.88 (3)	1.12 (4)	0.97 (12)
C(13)–H(12)	0.96 (3)	1.05 (4)	0.99 (5)

(i) $1-x, \bar{y}, 2-z$ for (I); $1-x, 1-y, 1-z$ for (II).

cations, must concern some minor details in the molecular conformation. A comparison of the two molecular geometries was thus carried out with recourse to the probability-plot analysis (Abrahams & Keve, 1971) which was performed following De Camp (1973) with all the independent bonded and non-bonded (these last being most sensitive to conformational changes) interatomic distances <7.50 Å, with the exclusion of those to hydrogen atoms. The resulting half-normal probability plot is shown in Fig. 2; all the points lie nearly on a straight line.* The linearity is much improved by omitting the three extreme points, thus reducing the maximum $(\Delta/\sigma)_{\text{obs}}$ from 9.11 to 5.89. These three points represent non-bonded distances to C(13) involving the C(1)–C(6) phenyl ring. In Figs. 3 and 4, the molecular packing is depicted for (I)

* Number of distances = 91. Maximum $(\Delta/\sigma)_{\text{obs}} = 9.11$. Slope = 2.86. Intercept = 0.35. Correlation coefficient = 98.2%.

Table 3. Bond angles ($^\circ$) for the two compounds together with the weighted mean

	(I)	(II)	Weighted mean
C(1)–P–C(7)	101.3 (3)	100.7 (4)	101.1 (4)
C(1)–P–C(13)	100.1 (3)	100.8 (3)	100.4 (4)
C(7)–P–C(13)	102.6 (3)	103.2 (6)	102.7 (4)
P–C(1)–C(2)	119.0 (5)	118.9 (7)	119.0 (4)
P–C(1)–C(6)	123.2 (5)	122.6 (5)	122.9 (5)
P–C(7)–C(8)	116.7 (6)	115.7 (8)	116.3 (7)
P–C(7)–C(12)	125.6 (6)	126.1 (6)	125.8 (5)
C(2)–C(1)–C(6)	117.8 (7)	118.5 (6)	118.2 (6)
C(1)–C(2)–C(3)	120.7 (7)	120.2 (9)	120.5 (6)
C(2)–C(3)–C(4)	120.3 (9)	120.2 (8)	120.2 (6)
C(3)–C(4)–C(5)	120.2 (9)	120.3 (8)	120.3 (6)
C(4)–C(5)–C(6)	119.9 (7)	119.9 (9)	119.9 (5)
C(5)–C(6)–C(1)	121.0 (6)	120.8 (7)	120.9 (5)
C(8)–C(7)–C(12)	117.6 (8)	118.0 (8)	117.8 (6)
C(7)–C(8)–C(9)	120.0 (11)	119.6 (10)	119.8 (8)
C(8)–C(9)–C(10)	122.1 (13)	122.0 (11)	122.0 (8)
C(9)–C(10)–C(11)	118.8 (14)	119.1 (12)	119.0 (9)
C(10)–C(11)–C(12)	120.5 (12)	120.0 (11)	120.2 (8)
C(11)–C(12)–C(7)	120.9 (9)	121.3 (8)	121.1 (6)
P–C(13)–C(13 ^b)	111.1 (4)	110.6 (6)	110.9 (4)

(i) $1-x, \bar{y}, 2-z$ for (I); $1-x, 1-y, 1-z$ for (II).

Table 4. Torsion angles ($^\circ$) for the two compounds

The torsion angle designation corresponds to the right-hand rule (Klyne & Prelog, 1960).

	(I)	(II)
C(1)–P–C(13)–C(13 ^b)	–70.0 (3)	69.7 (2)
C(7)–P–C(13)–C(13 ^b)	–174.1 (2)	173.6 (2)
C(2)–C(1)–P–C(13)	109.1 (3)	–111.8 (3)
C(6)–C(1)–P–C(13)	–70.0 (3)	69.4 (3)
C(8)–C(7)–P–C(13)	173.2 (3)	–173.8 (3)
C(12)–C(7)–P–C(13)	–10.3 (4)	10.8 (3)
C(1)–P–C(7)–C(8)	70.0 (3)	–69.9 (3)
C(6)–C(1)–P–C(7)	35.2 (3)	–36.4 (3)

(i) $1-x, \bar{y}, 2-z$ for (I); $1-x, 1-y, 1-z$ for (II).

and (II) respectively, while the most significant intermolecular contacts, all less than 3.7 Å, are quoted in Table 5 for both compounds.

Some slight structural differences are also evident by comparing the vibrational absorption bands of the two forms. These differences involve the shape of the bands rather than frequencies and, in particular, some vibrational modes of the phenyl rings.

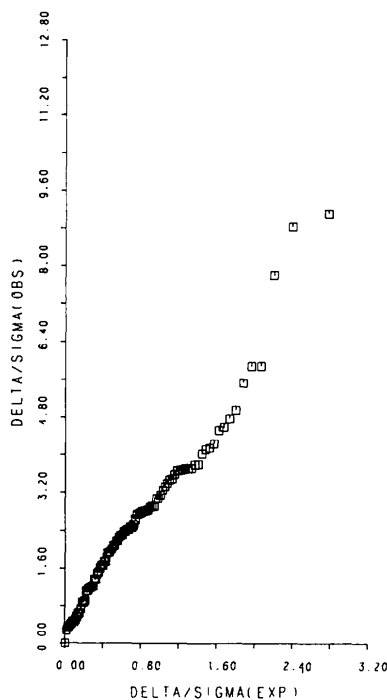


Fig. 2. Half-normal probability plot.

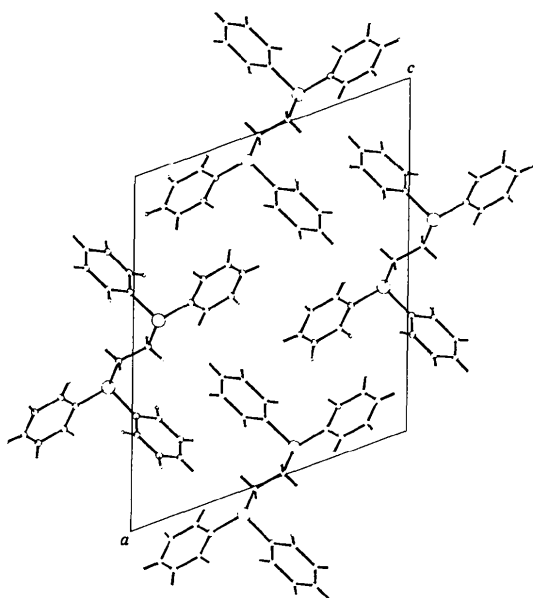


Fig. 3. Compound (I). Diagrammatic projection along $[010]$ showing molecular packing.

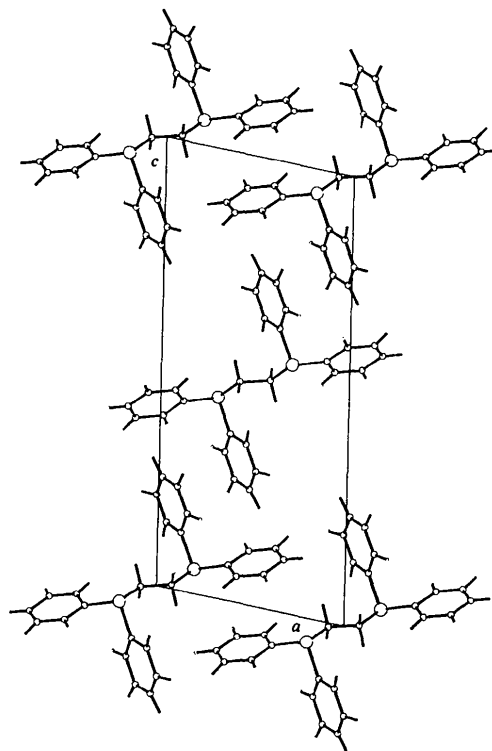


Fig. 4. Compound (II). Diagrammatic projection along $[0\bar{1}0]$ showing molecular packing.

Table 5. Significant intermolecular contacts (Å)

Compound (I)			
C(2) ⁱ ...C(6 ⁱⁱ)	3.701 (6)	C(8 ⁱ)...C(11 ⁱⁱ)	3.583 (8)
Compound (II)			
C(8 ⁱ)...C(11 ⁱⁱ)	3.580 (8)	C(7 ⁱ)...C(11 ^v)	3.552 (6)
C(4 ⁱ)...C(6 ⁱⁱⁱ)	3.648 (5)	C(11 ⁱ)...C(12 ^v)	3.618 (7)
C(3 ⁱ)...C(9 ^{iv})	3.658 (7)	C(12 ⁱ)...C(12 ^v)	3.531 (6)
(i) $x, y, z;$		(iv) $1 + x, y, z;$	
(ii) $x, 1 + y, z;$		(v) $\bar{x}, 1 - y, 1 - z.$	
(iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$			

Finally, structural data as well as the half-normal probability plot support the hypothesis that the conformations of the molecules are practically identical and that the differences which appeared in the infrared spectra are mainly due to different packing modes.

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Alkaloids of *Veratrum album* subspecies *lobelianum* (Bernh.) Suessenguth. XXX.* Structure of *O*-Acetylveramarine

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Abstract

$C_{29}H_{45}NO_4$, $M_r = 471.7$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 6.342$ (2), $b = 20.961$ (11), $c = 19.809$ (6) Å, $U = 2633.3$ Å³, $D_m = 1.14$ (8), $D_x = 1.19$ Mg m⁻³, $\mu(\text{Cu } K\alpha, \lambda = 1.5418 \text{ Å}) = 0.62 \text{ mm}^{-1}$. The structure was solved by direct methods and refined by least squares to an R of 0.044 on the basis of 1501 independent counter intensities. The three O substituents on the cevanine skeleton are on the β side, and the rings are *trans*-fused in pairs, except for the middle five- and six-membered rings which are *cis*-fused. There is strong evidence for intramolecular O–H...O–H...N hydrogen bonds with H...O = 2.02 and H...N = 2.19 Å.

Introduction

The alkaloid veramarine, a minor alkaloid from *Veratrum album* subspecies *lobelianum* (Bernh.), was isolated by Tomko & Vassová (1965). Its chemical

configuration was established (Tomko, Votický, Budzikiewicz & Durham, 1965) and its stereochemistry proposed (Itô, Ogino & Tomko, 1968) on the basis of its chemical reactivity, physico-chemical measurements and a consideration of the biogenesis of the *C*-nor-*D*-homo steroidal skeleton. Feeling the need for more substantial proof of this proposal we have examined *O*-acetylveramarine by X-ray crystallography (since veramarine is amorphous).

Experimental

The crystal used for structure determination was of prismatic form {100}, {010}, {011} with approximate dimensions 0.25 × 0.15 × 0.05 mm. The density was measured by flotation in aqueous KI solution. The space group and unit-cell data were obtained from rotation and Weissenberg photographs. Unit-cell parameters were refined by a least-squares fit of seven independent reflections measured on the diffractometer. The intensities of 2085 reflections (up to $2\theta = 115^\circ$) were collected on a four-circle fully automated

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