filled $2p$ orbital of the C(1) atom and the vacant d orbital of the I atom probably occurs similarly to that in phosphorus ylides (Johnson, 1966). The evidence for the assumption of orbital overlap has been provided from the fact that the C(1)—I bond is shorter than C(5)—I. The S(1)—C(1) and S(2)—C(1) bonds are obviously shorter than S(1)—C(2) and S(2)—C(4). The bond retrenchment reveals that the O═S—C$^-$ structure probably changes into its resonance structures O(1)$^-$—S(1)═C(1), O(2)$^-$—S(1)═C(1), O(3)$^-$—S(2)═C(1) and O(4)$^-$—S(2)═C(1) because the bonds C(1)—S(1) and C(1)—S(2) represent a double bond in four resonance structures. Clearly, the resonances delocalize the negative charge of the carbanion C(1), thereby stabilizing the carbanion structure and leading to an easy crystallization of the title compounds at room temperature. However, some phenyliodonium ylides containing sulfonyl groups without CF_2 groups are unstable at room temperature (Hatjiarapoglou & Varvoglis, 1988). Based on the above fact, it can be considered that the strong electron attraction of adjacent CF_2 groups aggravates the electron deficiency of the SO_2 group and therefore the SO_2 group tends to accept an electron from the carbanion by resonance. A similar situation has been found in some phosphorus ylides with a carbonyl group (Fliszar, Hudson & Salvadori, 1963; Johnson, 1966). Structure (II) consists of a title ylide molecule and an Me_2SO molecule. The configuration of the ylide in the crystal is generally consistent with that of (I) but the precision of structural parameters of the former seems better than that of the latter due to the crystal quality. The shortest contact between the ylide and Me_2SO is I—O(5) at 2·564 (4) Å. This distance implies that the interaction between the ylide and Me_2SO is different from a van der Waals interaction by which host molecules usually interact with solvent molecules in most crystals. It can be inferred that the I atom can either as an electron donor coordinate with the C(1) atom or as an acceptor receive the lone-pair electrons from O(5) atoms to form a charge-transfer complex (Cotton, 1972; Foster, 1973). The C(1)—I···O(5) bond angle [176·1 (2)°] shows a linear linkage among the three atoms. This type of charge-transfer bonding behaviour is similar to that in the complex of 1,4-dioxane with iodine monochloride in which the O···I distance = 2·57 Å and the O···I—Cl system is linear (Hassel & Hvoslef, 1956).

References

B. A. Frenz & Associates Inc. (1984). *SDP-Plus Structure Determination Package*. College Station, Texas, USA.

Chen, Q.-Y. (1991). In preparation.

Cotton, F. A. (1972). *Advanced Inorganic Chemistry*, pp. 563–564. New York: Interscience.

Fliszar, S., Hudson, R. F. & Salvadori, G. (1963). *Helv. Chim. Acta*, **46**, 1580–1584.

Foster, R. (1973). *Molecular Complexes*, pp. 164–166. London: Elck Science.

Hassel, O. & Hvoslef, J. (1956). *Acta Chem. Scand.* **10**, 138–141.

Hatjiarapoglou, L. & Varvoglis, A. (1988). *J. Chem. Soc. Perkin Trans.* 1, pp. 2839–2846.

Johnson, A. W. (1966). *Ylid Chemistry*, pp. 1–4, 65–67, 80–82. New York: Academic Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Schmidbaur, H. (1973). *Chem. Ber.* **106**, 1251–1255.

Acta Cryst. (1991). C**47**, 1230–1234

Structure of a Chiral Tricyclic Phosphonamide

By Youssef L. Bennani and Stephen Hanessian*

Department of Chemistry, Université de Montréal, CP 6128, *Succ. A, Montréal, Québec, H*3*C* 3*J*7, *Canada*

(*Received* 29 *March* 1990; *accepted* 18 *September* 1990)

Abstract. 2-[1-(1,3-Dithiolan-2-ylideneamino)-3-butenyl]-2,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1H-1,3,2-benzodiazaphosphole 2-oxide, $C_{15}H_{26}N_3OPS_2$, $M_r = 359{\cdot}48$, trigonal, $P3_121$, $a = b = 9{\cdot}778$ (7), $c = 34{\cdot}214$ (1) Å, $V = 2832{\cdot}9$ Å^3, $Z = 6$, $D_x = 1{\cdot}264$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 3{\cdot}37$ mm^{-1}, $F(000) = 3552$, $T = 190$ K, $R = 0{\cdot}046$ for 1991 observed reflections. The title compound contains two heterocyclic rings, a 1,3-diazaphosphole 2-oxide and a 1,3-dithiolanylideneaminobutene bonded to the P atom which is tetrahedrally coordinated. Both five-membered rings are in the half-chair conformation. The diaza ring is *trans*-fused to a cyclohexane which is in the chair conformation. The

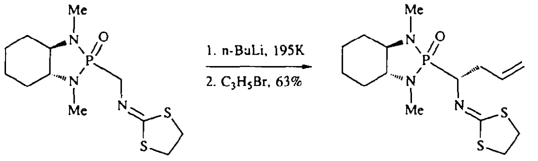
---

* Author to whom correspondence should be addressed.

0108-2701/91/061230-05$03.00

absolute configuration at the carbon center α to phosphorus is *R*.

Introduction. Chiral non-racemic α-aminoalkylphosphonamides can be obtained by alkylation of the corresponding 1,3-dithiolanylideneaminomethyl carbanions at low temperature (Hanessian & Bennani, 1990). Although the structures of the products can be proved by chemical and spectroscopic methods, we resorted to X-ray analysis to confirm the stereochemistry at the carbon α to phosphorus. The crystal structure of a phosphorus-stabilized carbanion was recently elucidated (Denmark & Dorow, 1990). We now report the crystal structure of the product (2) resulting from the treatment of tricyclic phosphonamide (1) with base followed by alkylation with allyl bromide.



(1) (2)

The alkylation of carbanions derived from alkyl (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986) and chloromethyl (Bélanger-Gariépy, Bennani, Hanessian & Brisse, 1989) bicyclic phosphonamides of the (*R*,*R*) configuration affords products having the opposite stereochemistry compared to the products obtained from the alkylation of (1) as depicted in (2).

Experimental. Crystals of $C_{15}H_{26}N_3OPS_2$ recrystallized from hexane, dimensions $0{\cdot}20 \times 0{\cdot}24 \times 0{\cdot}42$ mm. Unit-cell dimensions from 25 well centered reflections in the range $20{\cdot}5 \leq 2\theta \leq 22°$. Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, ω-scan mode, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14\tan\theta)°$, $2\theta_{\max} = 140{\cdot}0°$, limiting Miller indices: $0 \leq h \leq 11$, $0 \leq k \leq 11$ and $-41 \leq l \leq 41$. Orientation monitored every 200 measurements, intensities of six standard reflections (checked every hour) showed the largest fluctuation of ± 1·0%. 4279 measured reflections giving 2114 independent reflections after averaging ($R_{\text{ave}} = 0{\cdot}02$) of which 1991 with $I \geq 1{\cdot}96\sigma(I)$ were retained for structure determination and refinement. Lp and absorption correction performed (grid 10 × 10 × 10, transmission factors: 0·42–0·59). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and difference Fourier calculation *SHELX*76 (Sheldrick, 1976). Refinement based on *F* using full-matrix least squares, all non-H atoms anisotropic and H atoms isotropic. H atoms found on difference Fourier synthesis isotropically refined. Final $R = 0{\cdot}046$ (weights derived from the counting statistics), $w = 1/\sigma^2(F)$ and $S = 1{\cdot}24$ for 303 refined parameters. Maximum $(\Delta/\sigma) = 0{\cdot}33$, average $(\Delta/\sigma) = 0{\cdot}02$, residual electron density fluctuations on final difference Fourier synthesis showing four peaks of 0·82–0·20 e Å^{-3} at 0·76–0·95 Å from S atoms, background ranging from −0·42 to 0·20 e Å^{-3}.

Table 1. *Atomic coordinates* ($\times 10^4$, S *and* P $\times 10^5$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^4$) *for* $C_{15}H_{26}N_3OPS_2$

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S(1)	86709 (14)	13218 (17)	11858 (3)	48
S(2)	74176 (16)	4625 (21)	3865 (4)	60
P	37784 (13)	9884 (14)	6454 (3)	35
O	2170 (4)	200 (4)	475 (1)	49
N(1)	4142 (4)	2284 (5)	1001 (1)	38
N(2)	5292 (4)	2222 (4)	371 (1)	36
N(3)	5643 (4)	130 (4)	1039 (1)	36
C(1)	5774 (6)	3619 (5)	961 (1)	40
C(2)	6131 (7)	5170 (6)	1148 (2)	59
C(3)	7860 (8)	6393 (7)	1054 (2)	72
C(4)	8214 (7)	6548 (6)	622 (2)	68
C(5)	7733 (6)	4952 (6)	430 (2)	56
C(6)	6000 (5)	3831 (5)	522 (1)	40
C(7)	5220 (7)	2029 (7)	− 53 (1)	56
C(8)	3542 (7)	1762 (7)	1397 (1)	55
C(9)	4225 (5)	− 552 (5)	796 (1)	37
C(10)	2814 (6)	− 1935 (6)	1001 (2)	53
C(11)	3083 (7)	− 3282 (7)	1087 (2)	65
C(12)	2423 (9)	− 4329 (8)	1334 (2)	90
C(13)	6978 (5)	541 (5)	888 (1)	37
C(14)	10116 (6)	1971 (7)	798 (2)	54
C(15)	9411 (5)	875 (6)	456 (1)	44

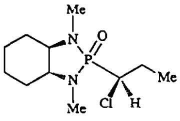
The scattering curves for the non-H atoms were taken from Cromer & Waber (1965) and those for the H atoms from Stewart, Davidson & Simpson (1965). The absolute configuration of $C_{15}H_{26}N_3OPS_2$ was established using the real and imaginary parts of anomalous dispersion of the P atom (Cromer & Liberman, 1970). Structure-factor calculations were performed for each configuration by changing the space group to $P3_221$ and x, y, z into $-x$, $-y$, $-z$. After one refinement cycle for the other configuration: $R = 0{\cdot}056$ and $S = 1{\cdot}56$. The ratio ($R = 1{\cdot}211$) is clearly larger than 1·0 (Hamilton, 1965). The final atomic coordinates for $C_{15}H_{26}N_3OPS_2$, given in Table 1,* are those of the unambiguously established absolute configuration based on the known stereochemistry of the (*R*,*R*)-*N*,*N*′-dimethyldiaminocyclohexane moiety and on the smaller values of *R* and *S*.

---

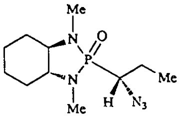
* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, distances and angles related to the H atoms, and a stereoview of the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53585 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. An *ORTEP* (Johnson, 1965) drawing showing a stereopair of the molecular conformation and the atom numbering is given in Fig. 1. The bond distances, angles and torsion angles, calculated from the final refined coordinates are given in Table 2. The absolute configuration of the newly formed stereogenic center resulting from the alkylation of (1) is secured from the X-ray data in view of the known stereochemistry of the parent diaminocyclohexane.

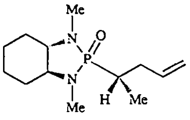
Compound (2) contains a cyclohexane ring (*A*) which is *trans*-fused to a 1,3-diazaphosphole oxide moiety (*B*). The 1-(1,3-dithiolan-2-ylideneamino)-3-butenyl chain is covalently attached to the tetrahedrally coordinated P atom. The torsion angles in ring *B* and in the 1,3-dithiolane ring (*C*) of compound (2) are compared to those in 1-chloropropyl (3) (Bélanger-Gariépy *et al.*, 1989), 1-azidopropyl (4) (Bennani, Bélanger-Gariépy & Hanessian, 1990) and 1-methyl-3-butenyl (5) (Bélanger-Gariépy *et al.*, 1986) bicyclic phosphonamides. Comparisons with values computed by Pitzer & Donath (1959) for the two minimum-energy conformations of cyclopentane are shown in Table 3.



(3)



(4)



(5)

Table 2. *Bond distances* (Å), *angles and torsion angles* (°) *for* $C_{15}H_{26}N_3OPS_2$

S(1)—C(13)	1·760 (5)	N(3)—C(9)	1·461 (7)
S(1)—C(14)	1·806 (6)	N(3)—C(13)	1·268 (7)
S(2)—C(13)	1·780 (4)	C(1)—C(2)	1·517 (7)
S(2)—C(15)	1·798 6)	C(1)—C(6)	1·517 (6)
P—O	1·482 (4)	C(2)—C(3)	1·540 (10)
P—N(1)	1·662 (4)	C(3)—C(4)	1·508 (10)
P—N(2)	1·656 (4)	C(4)—C(5)	1·534 (8)
P—C(9)	1·839 (5)	C(5)—C(6)	1·521 (8)
N(1)—C(1)	1·479 (7)	C(9)—C(10)	1·536 (7)
N(1)—C(8)	1·463 (6)	C(10)—C(11)	1·496 (9)
N(2)—C(6)	1·460 (6)	C(11)—C(12)	1·232 (9)
N(2)—C(7)	1·460 (6)	C(14)—C(15)	1·501 (7)
C(13)—S(1)—C(14)	97·4 (3)	C(1)—C(2)—C(3)	107·6 (5)
C(13)—S(2)—C(15)	97·0 (2)	C(2)—C(3)—C(4)	113·0 (6)
O—P—N(1)	116·9 (2)	C(3)—C(4)—C(5)	112·3 (6)
O—P—N(2)	119·0 (2)	C(4)—C(5)—C(6)	108·0 (5)
O—P—C(9)	108·0 (2)	N(2)—C(6)—C(1)	104·2 (4)
N(1)—P—N(2)	95·0 (2)	N(2)—C(6)—C(5)	117·4 (4)
N(1)—P—C(9)	111·8 (2)	C(1)—C(6)—C(5)	109·7 (4)
N(2)—P—C(9)	105·3 (2)	P—C(9)—N(3)	110·2 (3)
P—N(1)—C(1)	109·3 (3)	P—C(9)—C(10)	111·9 (4)
P—N(1)—C(8)	121·1 (4)	N(3)—C(9)—C(10)	111·8 (4)
C(1)—N(1)—C(8)	117·5 (4)	C(9)—C(10)—C(11)	112·9 (5)
P—N(2)—C(6)	110·7 (3)	C(10)—C(11)—C(12)	128·1 (7)
P—N(2)—C(7)	120·1 (3)	S(1)—C(13)—S(2)	112·4 (3)
C(6)—N(2)—C(7)	117·2 (4)	S(1)—C(13)—N(3)	119·8 (4)
C(9)—N(3)—C(13)	120·3 (4)	S(2)—C(13)—N(3)	127·7 (4)
N(1)—C(1)—C(2)	116·8 (4)	S(1)—C(14)—C(15)	108·8 (4)
N(1)—C(1)—C(6)	103·4 (4)	S(2)—C(15)—C(14)	108·8 (4)
C(2)—C(1)—C(6)	109·5 (4)		
Ring *A*		Inter-ring	
C(1)—C(2)—C(3)—C(4)	54·9 (7)	P—N(1)—C(1)—C(2)	157·2 (4)
C(2)—C(3)—C(4)—C(5)	−53·4 (7)	P—N(2)—C(5)—C(5)	154·1 (4)
C(3)—C(4)—C(5)—C(6)	54·7 (7)	N(1)—C(1)—C(2)—C(3)	−177·5 (5)
C(4)—C(5)—C(6)—C(1)	−60·6 (6)	N(2)—C(6)—C(5)—C(4)	−179·2 (5)
C(5)—C(6)—C(1)—C(2)	65·9 (6)	C(8)—N(1)—C(1)—C(2)	−59·8 (6)
C(6)—C(1)—C(2)—C(3)	−60·4 (6)	C(7)—N(2)—C(6)—C(5)	−63·0 (6)
Ring *B*		Ring *C*	
P—N(1)—C(1)—C(6)	36·7 (4)	S(1)—C(14)—C(15)—S(2)	43·0 (5)
N(1)—C(1)—C(6)—N(2)	−42·4 (5)	C(14)—C(15)—S(2)—C(13)	−33·2 (4)
C(1)—C(6)—N(2)—P	32·7 (4)	C(15)—S(2)—C(13)—S(1)	11·5 (3)
C(6)—N(2)—P—N(1)	−10·3 (3)	S(2)—C(13)—S(1)—C(14)	9·1 (3)
N(2)—P—N(1)—C(1)	−16·5 (3)	C(13)—S(1)—C(14)—C(15)	−31·7 (4)
Others			
O—P—C(9)—N(3)	−168·0 (3)	P—C(9)—C(10)—C(11)	173·7 (4)
O—P—N(2)—C(7)	−27·4 (5)	C(9)—C(10)—C(11)—C(12)	157·9 (7)
O—P—C(9)—C(10)	−42·9 (4)		
O—P—N(1)—C(8)	75·9 (4)	P—C(9)—N(3)—C(13)	95·7 (5)
O—P—N(1)—C(1)	−142·7 (3)	C(9)—N(3)—C(13)—S(1)	−178·6 (3)
O—P—N(2)—C(6)	114·3 (3)	C(9)—N(3)—C(13)—S(2)	2·4 (7)
N(1)—P—C(9)—N(3)	−38·1 (4)	C(9)—P—N(1)—C(8)	−49·3 (5)
N(1)—P—C(9)—C(10)	87·0 (4)	C(9)—P—N(2)—C(7)	93·9 (4)
N(2)—P—C(9)—N(3)	63·8 (4)	C(9)—P—N(1)—C(1)	92·2 (4)
N(2)—P—C(9)—C(10)	−171·1 (3)	C(9)—P—N(2)—C(6)	−124·5 (3)

For phosphonamide (2), both the diaza and dithia five-membered ring torsion angles conform to those tabulated for the half-chair conformation of cyclopentane. The average deviations from the computed

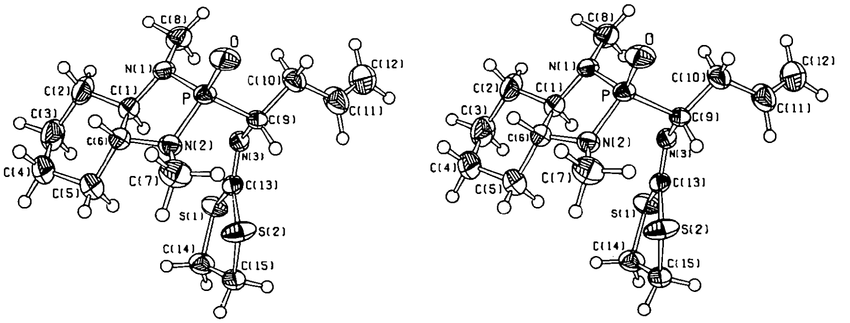


Fig. 1. *ORTEP* drawing of $C_{15}H_{26}N_3OPS_2$ showing the numbering scheme used for the structure. Atoms are represented at 50% probability level, H atoms are drawn by spheres of arbitrary size.

Table 3. *Torsion angles* (°) *for the five-membered rings B and C in compound* (2) (*this work*), (3) (*Bélanger-Gariépy et al.*, 1989), (4) (*Bennani et al.*, 1990), (5) (*Bélanger-Gariépy et al.*, 1986) *and computed values for the half-chair and the envelope conformations of cyclopentane* (*Pitzer & Donath*, 1959)

Ring *B*	(2)	(3)	(4)	(5)	Half-chair	Envelope
N(1)—C(1)—C(6)—N(2)	−42·4 (5)	−44·9 (0)	−44·0 (3)	41·2 (2)	−48·0	−46·1
C(1)—C(6)—N(2)—P	32·7 (4)	40·0 (6)	34·8 (3)	41·2 (2)	39·5	46·1
C(2)—N(2)—P—N(1)	−10·3 (3)	−20·1 (5)	−12·5 (2)	23·7 (2)	−15·2	−28·6
N(2)—P—N(1)—C(1)	−16·5 (3)	−8·1 (5)	−14·7 (2)	1·9 (2)	−15·2	0·0
P—N(1)—C(1)—C(6)	36·7 (4)	32·4 (6)	36·3 (3)	−25·7 (2)	39·5	28·6

Ring *C*					
S(1)—C(14)—C(15)—S(2)	43·0 (5)	C(15)—S(2)—C(13)—S(1)	11·5 (3)	C(13)—S(1)—C(14)—C(15)	−31·7 (4)
C(14)—C(15)—S(2)—C(13)	−33·2 (4)	S(2)—C(13)—S(1)—C(14)	9·1 (3)		

values for the half-chair conformation are only 4·2 (5)° for ring *B* and 5·7 (4)° for ring *C* while the average deviation from the values for the envelope conformation are 11·9 (9) and 9·1 (0)°, respectively. For compound (3), the conformation of the five-membered diazaphosphole oxide ring is between the half-chair and envelope conformations. The same ring exists in the half-chair conformation in compound (4) and in the envelope conformation in (5). It appears that the nature of the substituent at the carbon α to the phosphorus in the bicyclic phosphonamides (2)–(5) induces changes in the conformation of the diaza ring.

The torsion angle N(2)—P—N(1)—C(1) is the most affected, varying from 1·9 (2)° for compound (5) (envelope form) to −14·7 (2)° for compound (4) (half-chair form) and −16·7 (1)° for compound (2). In phosphonamide (2) ring *B* is *trans*-fused to a cylcohexane ring (*A*) and the torsion angles N(1)—C(1)—C(6)—N(2) and C(2)—C(1)—C(6)—C(5) are −42·4 (5) and 65·9 (6)°, respectively.

In the cyclohexane ring, C(2) and C(5) are symmetrically disposed with distances from the remaining four-atom plane at 0·705 (5) and −0·694 (1) Å, respectively. The endocylic torsion angles have an average of 58·3 (0)° showing a deviation from the 'standard' torsion angle, $\tau = 55{\cdot}8°$, for a cyclohexane ring in the chair conformation (Bucourt & Hainaut, 1965). The largest deviations involve the C(1)—C(6) bond which is also part of the five-membered ring. The mean value of the ring valency angles is 101.0 (6)° and the C—C distances average 1·523 Å.

The environment of the two N atoms of the five-membered ring is not planar. The distortion, measured by the three N-atom bond angles (∑N), indicates ∑N(1) = 347·9 (1)° and ∑N(2) = 348·1 (0)° instead of ∑N = 360° for a planar group. Consequently, N(1) and N(2) deviate from the plane formed by their three neighbours by 0·311 (5) and 0·307 (4) Å, respectively. Because of the influence of the P atom, the angles P—N(1)—C(8) and P—N(2)—C(7) with values of 121·1 (4) and 120·1 (3)°, respectively, are significantly larger than C(1)—N(1)—C(8) = 117·5 and C(6)—N(2)—C(7) = 117·2 (4)°.

The coordination at the P atom is approximately tetrahedral since the average of the six angles is 109·3 (5)°. However, the coordination is clearly distorted since the O—P—N bond angles, averaging 117·9 (7)°, are much larger than the N(1)—P—N(2) angle whose value is 95·0 (2)°. The presence of phosphorus in the five-membered ring might be responsible for such a distortion. The P—O bond length is 1·482 (4) Å, in good accordance with the P—O distances in the other bicyclic phosphonamides such as (3), (4) and (5) with values of 1·466 (4), 1·478 (4) and 1·472 (3) Å respectively. The P—C(9) bond distance is 1·839 (5) Å and the torsion angle O—P—C(9)—N(3) is −168·0 (3)° showing a distortion from a perfectly staggered conformation and that the O atom is *trans* to the amino group of the iminodithiolane ring. The absolute configuration at C(9) is *R*.

The five-membered dithiolane ring (*C*) is bonded at C(13) to N(3) and the bond distance of 1·268 (7) Å agrees with standard lengths for a C—N double bond. The average S—C(13) bond distance is 1·770 (4) Å, while the S—C(14) and S—C(15) distances are 1·806 (6) and 1·798 (6) Å, respectively, both being slightly larger than the bond distances in 1,3,2-dithiazole-4-thione (Oakley, Koenig & Cordes, 1987). For this ring (*C*), the average C—S—C angle is 97·8 (3)°. The torsion angle P—C(9)—N(3)—C(13) is −95·7 (5)°, indicating that the dithia ring is distorted towards N(2) which is at −0·307 (3) Å from the C(7)—C(6)—P plane.

We thank the 'Ministère de l'Éducation du Québec' for financial support of this research, and Dr M. Simard for assistance in the resolution of the structure.

References

Bélanger-Gariépy, F., Bennani, Y. L., Hanessian, S. & Brisse, F. (1989). *Acta Cryst.* C**45**, 289–291.

Bélanger-Gariépy, F., Delorme, D., Hanessian, S. & Brisse, F. (1986). *Acta Cryst.* C**42**, 856–860.

Bennani, Y. L., Bélanger-Gariépy, F. & Hanessian, S. (1990). *Acta Cryst.* C**46**, 653–656.
Bucourt, L. S. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.
Denmark, S. E. & Dorow, R. L. (1990). *J. Am. Chem. Soc.* **112**, 864–866.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
Hanessian, S. & Bennani, Y. L. (1990). *Tetrahedron Lett.* **31**, 6465–6468.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Oakley, R. T., Koenig, H. & Cordes, A. W. (1987). *Acta Cryst.* C**43**, 2468–2469.
Pitzer, K. S. & Donath, W. E. (1959). *J. Am. Chem. Soc.* **81**, 3213–3118.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1991). C**47**, 1234–1236

Phenyl-Substituted Cyclopropanes. II. Ethyl *trans*-2-Phenylcyclopropane-1-carboxylate

By Asiloé J. Mora, A. Valentina Rivera,* Eldrys Rodulfo de Gil and Miguel E. Alonso
Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, Venezuela

and Sarah Pékerar
Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela

(*Received* 30 *October* 1989; *accepted* 18 *September* 1990)

Abstract. $C_{12}H_{14}O_2$, $M_r = 190{\cdot}24$, orthorhombic, $Pca2_1$, $a = 6{\cdot}931$ (2), $b = 7{\cdot}708$ (2), $c = 20{\cdot}288$ (4) Å, $V = 1084$ Å^3, $Z = 4$, $D_x = 1{\cdot}17$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 408$, $T = 298$ K, $R = 0{\cdot}078$ for 398 unique reflections. The ester substituent adopts a *cis*-bisected conformation with the carbonyl oxygen eclipsing the ring. The phenyl substituent also adopts the bisected conformation and, hence, competes with the ester group in conjugative interactions with the cyclopropane ring. Ring bond lengths are equal at 1·50 (2), 1·50 (2), 1·51 (2) Å, the high e.s.d.'s being due to limitations placed on the room-temperature data set by the low melting point (311–312 K).

Introduction. The interaction between a cyclopropane ring and an appropriately oriented π-acceptor substituent, *e.g.* a carbonyl group, shortens the distal bond opposite the substituent and lengthens the vicinal bonds. Data for electron-donor substituents are sparse and their effects on the ring are not clearly defined. In the case of phenyl substituents they appear to accept electron density from the cyclopropane $3e'$ orbitals in the bisected conformation, but to donate electron density to the $4e'$ orbitals in the predominant perpendicular conformation (Allen, 1980). The many reported structures of phenylcyclopropanes are mostly heavily substituted (Yamamoto, Sakai, Ohta, Matsuzaki & Fukuyama, 1985; Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1985; Poppleton, 1986; Allen, 1980, and references therein). In these structures, along with the electronic interaction, there is always an added steric effect between the phenyl group and other substituents. We are currently examining some phenylcyclopropanes which exhibit minimum steric effects in order to understand the complex electronic interactions in phenyl-substituted cyclopropanes.

Here we report the structure of ethyl *trans*-2-phenylcyclopropane-1-carboxylate which, together with (*E*)-2-(*p*-nitrophenyl)cyclopropyl methyl ketone (Bordner, Jones & Johnson, 1972) and *trans*-2-(*p*-tolyl)cyclopropanoic acid (Ramírez, Rivera, Rodulfo de Gil, Alonso & Pékerar, 1990), are the only reported phenylcyclopropanes in the crystalline state with minimal steric effects. Consequently, the phenyl substituent might be expected to adopt the energetically preferred conformation.

Experimental. Elongated white prisms were grown from ether:hexane. Crystal 0·32 × 0·35 × 0·26 mm sealed in a Lindemann tube. Automated four-circle Philips PW 1100 diffractometer. Lattice parameters

---

* To whom correspondence should be addressed.

0108-2701/91/061234-03$03.00