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Structures of the *E* and *Z* Isomers of Methyl *N*-*tert*-Butyl-*N*-(2-cyano-1-methylthio-2-phenylvinyl)carbamate, $C_{16}H_{20}N_2O_2S$

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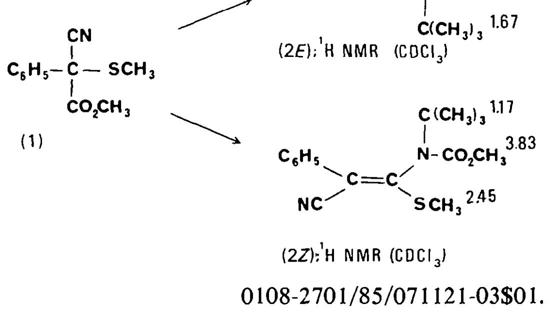
Abstract. *E* isomer: $M_r = 304{\cdot}4$, monoclinic, $P2_1/n$, $a = 8{\cdot}755\ (2)$, $b = 20{\cdot}802\ (3)$, $c = 9{\cdot}394\ (3)$ Å, $\beta = 93{\cdot}17\ (3)°$, $V = 1708{\cdot}2\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}18$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}186$ mm^{-1}, $F(000) = 648$, $T = 293$ K, $wR = 0{\cdot}060$ for 1631 reflexions. *Z* isomer: $M_r = 304{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}811\ (2)$, $b = 9{\cdot}432\ (2)$, $c = 11{\cdot}004\ (3)$ Å, $\alpha = 77{\cdot}19\ (3)$, $\beta = 75{\cdot}21\ (3)$, $\gamma = 71{\cdot}16\ (4)°$, $V = 827{\cdot}1\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}22$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\mu = 0{\cdot}192$ mm^{-1}, $F(000) = 324$, $T = 293$ K, $wR = 0{\cdot}036$ for 1795 reflexions. The N atom and the three C atoms bound to it are planar. The aromatic ring is twisted out of the plane of the double bond, as is the plane containing the N atoms; this twist angle is different for the two isomers. In the *Z* isomer the *tert*-butyl group is shielded by the phenyl ring and its ^{1}H NMR signal is shifted to a higher field compared with the *E* isomer.

Introduction. *tert*-Butyl isocyanide is inserted into the C—S bond of the sulphide (1) to give the *N*-vinylcarbamates (2*E*) and (2*Z*). The signal observed by ^{1}H NMR for the *tert*-butyl group is shifted to a higher field by 0·50 p.p.m. from (2*E*) to (2*Z*). It was assumed that this group, in the preferential conformation of the *Z* isomer, is shielded by the phenyl group, which is not in the plane of the olefinic system for steric reasons (Morel, Marchand, Nguyen Thi & Foucaud, 1984).



These unexpected NMR data have been sufficient to prompt us to initiate X-ray crystallographic analysis of (2*E*) and (2*Z*). Furthermore, knowledge of the conformation of the nitrogen atom was necessary for later studies.

Experimental. Enraf–Nonius CAD-4 automated diffractometer (Centre de Diffractométrie de l'Université de Rennes). Least-squares refinements of unit cells with 25 reflections.

(2*E*): intensity measurements: single crystal 0·2 × 0·35 × 0·4 mm, $\theta_{\max} = 28°$, scan $\omega/2\theta = 1$. Range of *hkl*: $\bar{1}\bar{1}$, 11; 0, 27; 0, 12. Standard reflexions (101, 022, $\bar{1}30$): ± 1·2%; 4489 reflexions measured, 3887 unique [1631 with $I > \sigma(I)$]. $R_{\rm int} = 0{\cdot}023$.

(2*Z*): intensity measurements: single crystal 0·3 × 0·3 × 0·4 mm, $\theta_{\max} = 28°$, scan $\omega/2\theta = 1$. Range of *hkl*: $\bar{1}\bar{1}$, 11; $\bar{1}\bar{2}$, 12; 0, 14. Standard reflexions (012, 004, 223): ± 1·4%. 4109 reflexions measured, 3911 unique [1795 with $I > 3\sigma(I)$]. $R_{\rm int} = 0{\cdot}016$.

Structures solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) with programs of *SDP* package (Frenz, 1978). All non-hydrogen atoms revealed with best set. Isotropic then anisotropic refinements, all hydrogen atoms of (2*E*) and (2*Z*) (respectively between densities 0·35 and 0·17, 0·43 and 0·28 e Å^{-3}) found. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final full-matrix refinement (on *F*) with $1/w = \nu^2/F = \frac{1}{4}|(\nu^2/I) + (0{\cdot}04)^2|$ gave for (2*E*): $wR = 0{\cdot}060$, $R = 0{\cdot}069$; for (2*Z*): $wR = 0{\cdot}036$, $R = 0{\cdot}050$. Max. peaks in final difference Fourier maps 0·17 for (2*E*) and 0·15 e Å^{-3} for (2*Z*). Max. Δ/σ 0·6 for (2*E*), 0·4 for (2*Z*) for non-hydrogen atoms.

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Discussion. Atomic parameters are given in Table 1.* Bond distances and angles for non-hydrogen atoms are in Table 2. Figs. 1 and 2 give perspective views of the two compounds. All these data agree with normal values.

In the two isomers, the atoms bound to the nitrogen are in a plane containing the nitrogen atom. The aromatic ring is not coplanar with the C(2)C(3)C(11) plane of the double bond. The observed angle of twist around the C(3)C(11) bond is 47·2 (2)° for (2*E*) and 43·1 (2)° for (2*Z*). In the case of (2*Z*), such an angle may be due to the position of the plane of the three atoms bound to the nitrogen, which shows a twist angle with the double-bond plane of 84·3 (2)°. This conformation results from the steric interaction between the *tert*-butyl and phenyl groups. In spite of its important steric requirement, the *tert*-butyl group lies near the phenyl group. In such a geometry, the *tert*-butyl group is shielded by the phenyl ring as is shown by the NMR spectrum. In the case of (2*E*), the important expansion of the *tert*-butyl group leads to a twist angle between the plane of the three atoms bound to the nitrogen and the C(2)C(3)C(11) plane of 91·9 (2)°, which is near to that of (2*Z*). A further point to note is that the interaction of the sulphur atom with the phenyl ring of (2*E*) gives a twist angle between the phenyl group and the plane

Table 1. *Positional parameters and their e.s.d.'s*

$B_{eq}(\text{Å}^2) = \frac{1}{2}\sum_i \sum_j B_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j$.

	Compound (2*E*)				Compound (2*Z*)			
	x	*y*	*z*	B_{eq}	*x*	*y*	*z*	B_{eq}
S	0·9571 (1)	0·21227 (5)	0·0283 (2)	4·85 (3)	0·05220 (7)	0·18829 (7)	0·38246 (6)	4·44 (1)
O(1)	1·2312 (4)	0·0486 (1)	−0·1584 (4)	7·59 (9)	0·2239 (2)	0·5071 (2)	0·0398 (1)	4·43 (4)
O(2)	1·1529 (4)	0·1448 (1)	−0·2401 (3)	5·71 (8)	0·2199 (2)	0·2655 (2)	0·0621 (1)	3·94 (4)
N(1)	1·5280 (4)	0·2235 (2)	−0·0688 (5)	6·5 (1)	0·3271 (3)	−0·1800 (2)	0·4167 (2)	5·38 (6)
N(2)	1·2049 (3)	0·1339 (1)	−0·0092 (3)	3·22 (7)	0·2634 (2)	0·3432 (2)	0·2240 (2)	3·05 (4)
C(1)	0·8614 (5)	0·1420 (3)	−0·0405 (6)	6·9 (1)	−0·0927 (3)	0·3348 (3)	0·3032 (2)	4·70 (6)
C(2)	1·1508 (4)	0·1984 (2)	−0·0013 (4)	3·05 (9)	0·2455 (2)	0·1994 (2)	0·2915 (2)	3·21 (5)
C(3)	1·2487 (4)	0·2474 (2)	−0·0169 (4)	3·20 (9)	0·3742 (3)	0·0748 (2)	0·2955 (2)	3·16 (5)
C(4)	1·4035 (5)	0·2326 (2)	−0·0459 (5)	4·3 (1)	0·3437 (3)	−0·0657 (2)	0·3638 (2)	3·80 (5)
C(5)	1·2603 (5)	0·0987 (2)	0·1251 (5)	4·0 (1)	0·2919 (3)	0·4560 (2)	0·2888 (2)	3·46 (5)
C(6)	1·2757 (7)	0·1442 (3)	0·2474 (6)	7·4 (2)	0·1383 (3)	0·5877 (3)	0·3100 (2)	4·61 (6)
C(7)	1·4164 (6)	0·0710 (3)	0·1075 (5)	7·0 (1)	0·4357 (3)	0·5112 (3)	0·2079 (2)	5·03 (6)
C(8)	1·1411 (7)	0·0472 (3)	0·1586 (7)	9·3 (2)	0·3347 (3)	0·3766 (3)	0·4163 (2)	4·91 (6)
C(9)	1·1987 (5)	0·1033 (2)	−0·1369 (5)	4·5 (1)	0·2340 (2)	0·3839 (2)	0·1032 (2)	3·22 (5)
C(10)	1·136 (1)	0·1183 (3)	−0·3876 (6)	13·8 (2)	0·1933 (3)	0·2926 (3)	−0·0656 (2)	4·97 (7)
C(11)	1·2129 (4)	0·3173 (2)	−0·0105 (4)	3·28 (9)	0·5503 (3)	0·0654 (2)	0·2433 (2)	3·26 (5)
C(12)	1·2640 (5)	0·3581 (2)	−0·1125 (5)	4·4 (1)	0·6066 (2)	0·1342 (3)	0·1224 (2)	4·52 (6)
C(13)	1·2380 (5)	0·4227 (2)	−0·1066 (5)	5·3 (1)	0·7699 (3)	0·1263 (3)	0·0817 (3)	5·23 (7)
C(14)	1·1635 (5)	0·4479 (2)	0·0030 (5)	5·5 (1)	0·8803 (3)	0·0504 (3)	0·1581 (3)	5·13 (7)
C(15)	1·1099 (5)	0·4089 (2)	0·1060 (5)	5·5 (1)	0·8272 (3)	−0·0204 (3)	0·2761 (2)	4·88 (6)
C(16)	1·1364 (5)	0·3430 (2)	0·1010 (5)	4·3 (1)	0·6643 (3)	−0·0131 (3)	0·3179 (2)	4·01 (6)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s*

	(2*E*)	(2*Z*)		(2*E*)	(2*Z*)
S(1)–C(1)	1·787 (5)	1·787 (2)	C(3)–C(11)	1·491 (4)	1·491 (2)
S(1)–C(2)	1·758 (3)	1·764 (2)	C(5)–C(6)	1·489 (6)	1·520 (3)
O(1)–C(9)	1·194 (4)	1·204 (2)	C(5)–C(7)	1·500 (6)	1·521 (3)
O(2)–C(9)	1·342 (4)	1·345 (2)	C(5)–C(8)	1·541 (6)	1·515 (2)
O(2)–C(10)	1·491 (6)	1·437 (2)	C(11)–C(12)	1·375 (5)	1·387 (2)
N(1)–C(4)	1·138 (4)	1·141 (2)	C(11)–C(16)	1·382 (5)	1·380 (2)
N(2)–C(2)	1·427 (4)	1·432 (2)	C(12)–C(13)	1·366 (5)	1·375 (3)
N(2)–C(5)	1·515 (4)	1·518 (2)	C(13)–C(14)	1·355 (6)	1·366 (3)
N(2)–C(9)	1·356 (4)	1·366 (2)	C(14)–C(15)	1·366 (6)	1·363 (3)
C(2)–C(3)	1·344 (4)	1·346 (2)	C(15)–C(16)	1·390 (5)	1·375 (3)
C(3)–C(4)	1·430 (5)	1·442 (2)			
C(1)–S(1)–C(2)	104·2 (2)	105·07 (9)	C(6)–C(5)–C(7)	106·5 (4)	108·4 (2)
C(9)–O(2)–C(10)	116·4 (4)	116·0 (1)	C(6)–C(5)–C(8)	109·5 (4)	108·9 (2)
C(2)–N(2)–C(5)	120·2 (3)	121·6 (1)	C(7)–C(5)–C(8)	112·8 (4)	111·1 (2)
C(2)–N(2)–C(9)	119·3 (3)	117·6 (1)	O(1)–C(9)–O(2)	123·7 (4)	123·6 (2)
C(5)–N(2)–C(9)	120·4 (3)	120·3 (1)	O(1)–C(9)–N(2)	126·8 (4)	125·8 (2)
S(1)–C(2)–N(2)	119·2 (2)	119·0 (1)	O(2)–C(9)–N(2)	109·5 (3)	110·6 (1)
S(1)–C(2)–C(3)	121·3 (2)	118·9 (1)	C(3)–C(11)–C(12)	119·7 (3)	123·2 (2)
N(2)–C(2)–C(3)	119·5 (3)	121·8 (1)	C(3)–C(11)–C(16)	121·4 (3)	119·4 (2)
C(2)–C(3)–C(4)	118·3 (3)	117·9 (2)	C(12)–C(11)–C(16)	128·8 (3)	117·5 (2)
C(2)–C(3)–C(11)	126·0 (3)	127·3 (1)	C(11)–C(12)–C(13)	121·0 (4)	120·3 (2)
C(4)–C(3)–C(11)	114·9 (3)	114·7 (1)	C(12)–C(13)–C(14)	120·1 (4)	121·2 (2)
N(1)–C(4)–C(3)	177·2 (4)	176·9 (2)	C(13)–C(14)–C(15)	120·4 (4)	119·1 (2)
N(2)–C(5)–C(6)	110·3 (3)	110·4 (1)	C(14)–C(15)–C(16)	119·8 (4)	120·2 (2)
N(2)–C(5)–C(7)	110·2 (3)	109·2 (1)	C(11)–C(16)–C(15)	119·7 (4)	121·6 (2)
N(2)–C(5)–C(8)	108·5 (3)	108·7 (1)			

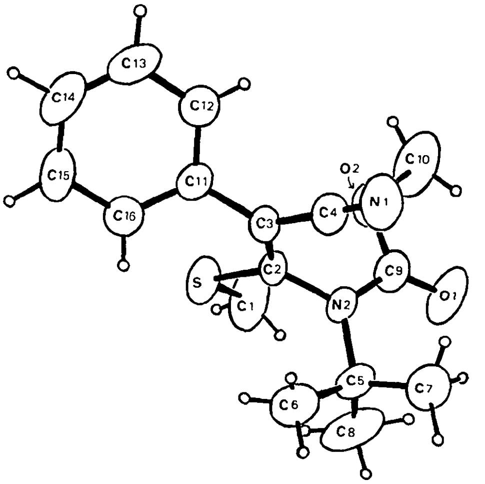

Fig. 1. *ORTEP* drawing (Johnson, 1965) of compound (2*E*) with atom labelling.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen parameters and bond distances involving hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42104 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(2)C(3)C(11) as important as that in (2*Z*). The distances between the methoxycarbonyl group and the phenyl ring or the cyano group are large enough to give no significant shielding or deshielding effect.

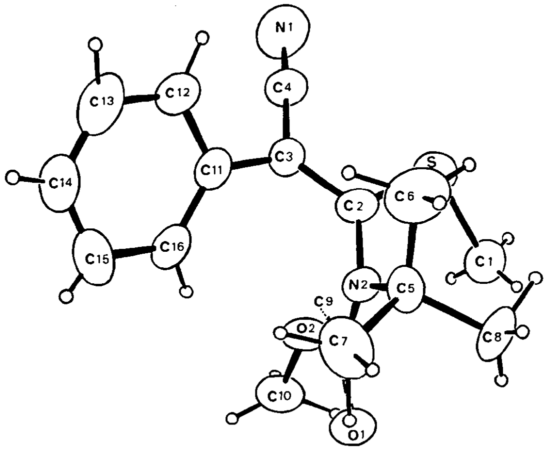

Fig. 2. *ORTEP* (Johnson, 1965) of compound (2*Z*) with atom labelling.

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Structure of 2′,3′,5′-Tri-*O*-acetylguanosine, $C_{16}H_{19}N_5O_8$

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Abstract. $M_r = 409{\cdot}4$, monoclinic, $P2_1$, $a = 7{\cdot}414$ (3), $b = 11{\cdot}491$ (4), $c = 11{\cdot}790$ (4) Å, $\beta = 99{\cdot}47$ (2)°, $U = 990{\cdot}75$ Å^3, $Z = 2$, $D_x = 1{\cdot}372$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}72$ cm^{-1}, $F(000) = 428$, $T = 293$ K, $R = 0{\cdot}053$ for 1241 unique reflections (Friedel pairs merged). The glycosidic torsion angle, χ, is $-160{\cdot}6$ (9)°, in the *anti* range, and the sugar pucker is C(2′)-*endo* (^2E), with $P = 167{\cdot}5$ (9)°, and $\psi_m = 28{\cdot}4$ (9)°. The C(4′)—C(5′) conformation is g^+, with $\gamma = 50{\cdot}8$ (9)°. There are three hydrogen bonds present, two of which base-pair symmetry-related molecules, O(6)···N(2) [2·94 (1) Å], N(7)···N(1) [2·86 (1) Å], and one is between the 5′-acetyl O atom and N(2) of a separate molecule [3·03 (1) Å]. Stacking involving the 2′-acetyl O atom between two base rings is noted.

Introduction. The structure was determined as part of our studies of nucleoside conformations, and solid-state interactions. Studies have been made of heavy-atom (halogenated) and, more recently, of acetyl-substituted pyrimidine nucleosides, which have brought to light interesting structural features. The present study continues this work, by investigating an acetyl-substituted purine nucleoside, designated TAG.

Experimental. Crystals were grown from aqueous solution, and were elongated along **a**. Cell dimensions obtained by diffractometry from crystals mounted along **a** and **b**. Intensity data collected from crystals mounted along **a** and **b**, with dimensions approximately 1·0 × 0·5 × 0·5 mm. Stoe Stadi II diffractometer (two-circle). Data collected from the *b*-axis crystal in the range $k = 0$ to 8, and from the *a*-axis crystal from $h = 0$ to 2, for scaling purposes. Max. $\sin\theta/\lambda$ 0·77 Å^{-1}. Range of indices: $-10 < h < 10$, $-14 < k < 14$, $-15 < l < 15$; No absorption corrections. One standard reflection measured every 100 reflections; intensity variation <5% from the mean. 6313 reflections measured; 2891 with $I < 3\sigma(I)$ regarded as unobserved; 1241 unique reflections used; $R_{\rm int} = 0{\cdot}042$. Structure solved by a combination of Patterson and direct methods. The orientation of the nine-membered purine base plane was obtained using the $I(\theta,\varphi)$ function of Tollin & Cochran (1964), which revealed the plane of the base ring, at $(\theta,\varphi) = (55°, 179°)$. This orientation agreed with that suggested by strong reflections $\bar{4}04$, $\bar{3}03$ and $\bar{2}02$. A one-dimensional rotation function (Tollin, 1976) carried out in this plane revealed the correct orientation of the base in this plane. The $I(\theta,\varphi)$ and rotation-function