

Fig. 1. An ORTEP (Johnson, 1965) plot of the host-guest complex (a) viewed through the mirror plane (the broken line indicates the mirror plane) and (b) viewed parallel to the plane of the guest molecule.

B are 58.5 (2) and 41.0 (2)°, respectively. The methyl group, C5X, of the guest was found to be directed towards the cavity. This methyl group penetrates directly and deeper into the cavity showing CH₃- π interaction between the guest and the host molecule. This interaction could be between the π electrons of the aromatic ring of the host molecule and the methyl group of the guest molecule. Also likely to be a factor in the interaction is the presence of the O2 atom of the host molecule. The introduction of this O atom widens the space of the 'cone' shape to produce the ellipsoidal cavity which nicely fits the molecular dimensions of the guest molecule, and also

indicates the possible interaction with the C5X methyl group of the guest molecule: a C—H...O interaction. This particular C—H...O interaction may be a very important key for the separation of the structural isomers of the guest molecules by the extractive crystallization with calixarenes, which shows about 73% extraction for *m*-xylene (Vicens, Armah, Fujii & Tomita, 1991). In the *m*-xylene molecule, disorder was observed. Several high thermal parameters (Table 1) probably result from the disorder, which may be the reason for the high *R* value.

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Structure of a Highly Substituted Pyrazolidin-3-one

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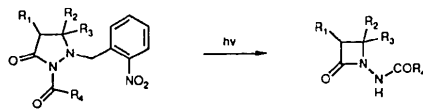
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Abstract. Trimethylsilylethyl *cis*-4,5-dimethyl-1-(*o*-nitrobenzyl)-3-oxopyrazolidine-2-carboxylate, C₁₈H₂₇N₃O₅Si, *M_r* = 393.51, triclinic, *P* $\bar{1}$, *a* = 11.237 (3), *b* = 13.073 (2), *c* = 8.040 (3) Å, α = 106.40 (2), β = 105.48 (2), γ = 85.70 (2)°, *V* = 1092.0 (5) Å³, *Z* = 2, *D_x* = 1.20 Mg m⁻³, λ (Mo *K* α) = 0.71069 Å, μ = 1.32 mm⁻¹, *F*(000) = 420, *T* = 296 K, *R* = 0.063, *wR* = 0.083 for 1970 observed unique reflections. The observed structure establishes

the relative stereochemistry between the C2 and C3 methyl groups as *cis*. The nitro group is twisted out of the plane containing the phenyl ring by 32.7 (7)°, and the N1—N2 bond distance of 1.435 (4) Å is representative of an N—N single bond.

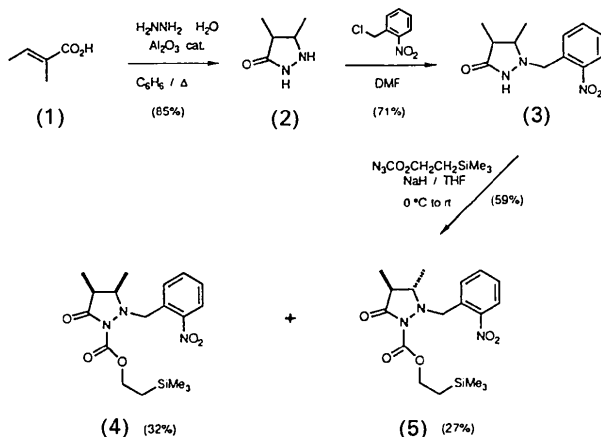
Introduction. The clinical importance of antibiotics containing a β -lactam ring has led to intense study of the reactivity and synthesis of compounds

incorporating this unique structure (Morin & Gorman, 1982). During the course of a recent study offering a general approach to the synthesis of monocyclic β -lactams (Florey, 1988) *via* photochemical ring contraction of pyrazolidin-3-ones to *N*-aminoazetidiones (Perri, Slater, Toske & White, 1990) (see scheme below), an ambiguity arose in the



Photochemical ring contraction

assignment of the configuration of two stereoisomeric pyrazolidin-3-ones. Prepared by the condensation of tiglic acid (1) with hydrazine, pyrazolidin-3-ones (2) were obtained as an inseparable mixture of *cis* and *trans* stereoisomers. After selective alkylation at N2 to afford (3), followed by acylation at N1, stereoisomers (4) and (5) could be separated by column chromatography. However, spectroscopic methods did not permit assignment of relative stereochemistry to (4) or (5). Since one of the isomers was available as a crystalline substance suitable for analysis by X-ray crystallography, its stereostructure was solved by this technique. Herein we report the stereochemistry of this compound as *cis*-4,5-dimethylpyrazolidin-3-one (4), and we comment on other structural features associated with (4) in the solid state.



Experimental. A colorless crystal of dimensions $0.2 \times 0.3 \times 0.4$ mm was grown from ether/hexane. D_m was not measured. Data were collected at 296 K by using a Rigaku AFC-6R diffractometer with graphite monochromator. Unit-cell parameters were determined using 20 centered reflections ($30.1 \leq 2\theta \leq 35.9^\circ$). Absorption was ignored. $(\sin\theta/\lambda)_{\max} = 0.594 \text{ \AA}^{-1}$; range of hkl : $0 \leq h \leq 12$, $-15 \leq k \leq 15$, $-9 \leq l \leq 8$. Three standard reflections observed

every 150 reflections showed an average variation in intensity of 1.3%. Intensities were measured in ω -2 θ mode at $16.0^\circ \text{ min}^{-1}$ in ω . 3264 unique reflections were measured, of which 1970 were observed [$F_o^2 > 3\sigma(F_o)^2$].

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983) and *DIRDIF* (Beurskens, 1984). H atoms were located in difference maps, placed at idealized positions and refined isotropically with B values of 1.2 times the value of B of the bonded atom. $\sum w(F_o - F_c)^2$ was minimized where $w = 1/\sigma^2(F_o)$. Anisotropic refinement of all non-H atoms converged at $R = 0.063$, $wR = 0.083$ and $S = 2.12$ with $(\Delta/\sigma)_{\max} = 0.003$ in the final cycle. The largest peaks in the final difference map were 0.61 and -0.30 e \AA^{-3} . Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs used are part of the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989).

Discussion. The final positional parameters and equivalent isotropic temperature factors for the non-H atoms are given in Table 1.* The atom-numbering scheme and molecular conformation of (4) are illustrated in Fig. 1. Bond distances and angles for the non-H atoms are listed in Table 2. The results indicate some rotational disorder of the trimethylsilyl group.

Fig. 2 provides a view of the structural features associated with the *o*-nitrobenzyl group in (4). The torsion angle defined by O4—N3—C14—C15 is $32.7(7)^\circ$. This rotation is smaller than the corresponding angle of 54.3° in *o*-nitrobenzoic acid (Tavale & Pant, 1973) but considerably larger than the angle of 4.8° in *p*-nitrotoluene (Barve & Pant, 1971). Calculation of intramolecular distances between various atoms in the vicinity of atom O5 reveals, through two significant interactions, the steric congestion that contributes to the rotation of the nitro group. The first is an unusually short distance of 2.275 \AA between atom O5 and one of the C12 benzylic H atoms. The second involves the H atom attached to atom C3 of the pyrazolidinone ring which is located at a distance of 2.545 \AA from atom O5. Evidence for a strong interaction between O5 and the benzylic H atom is revealed by the N3—C14—C13—C12 torsion angle of $8.0(7)^\circ$. This departure from planarity is accompanied by an expansion of the C12—C13—C14 bond angle to $127.3(4)^\circ$ and complementary compression of the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55032 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0564]

Table 1. Positional parameters and equivalent isotropic thermal factors (Å²) for C₁₈H₂₇N₃O₅Si
$$B_{eq} = (8\pi^2/3)\sum_j U_{jj} a_j^* a_j \cdot a_j$$

	x	y	z	B _{eq}
Si1	0.3079 (2)	0.8937 (1)	0.6181 (3)	6.69 (8)
O1	-0.0944 (3)	0.3589 (3)	0.0435 (5)	6.4 (2)
O2	-0.0246 (3)	0.5651 (3)	0.2711 (5)	6.5 (2)
O3	0.1813 (3)	0.5859 (2)	0.3533 (4)	4.7 (1)
O4	0.4829 (4)	0.2412 (4)	-0.2762 (6)	8.4 (2)
O5	0.3447 (4)	0.2133 (4)	-0.1602 (6)	8.9 (2)
N1	0.1025 (3)	0.4277 (3)	0.1838 (5)	3.6 (1)
N2	0.2275 (3)	0.3902 (3)	0.2016 (5)	3.4 (1)
N3	0.4350 (4)	0.2619 (4)	-0.1530 (6)	5.3 (2)
C1	0.0166 (4)	0.3478 (4)	0.0826 (7)	4.4 (2)
C2	0.0894 (4)	0.2470 (4)	0.0363 (7)	4.7 (2)
C3	0.2128 (4)	0.2743 (3)	0.1739 (7)	4.0 (2)
C4	0.0193 (6)	0.1485 (5)	0.022 (1)	8.0 (3)
C5	0.2178 (5)	0.2533 (4)	0.3505 (9)	6.5 (3)
C6	0.0770 (4)	0.5313 (4)	0.2723 (7)	4.2 (2)
C7	0.1690 (5)	0.6981 (4)	0.4440 (8)	5.8 (2)
C8	0.2929 (6)	0.7478 (4)	0.4974 (8)	6.0 (3)
C9	0.4763 (8)	0.9273 (6)	0.707 (1)	11.0 (4)
C10	0.237 (1)	0.9692 (7)	0.464 (2)	22.9 (8)
C11	0.247 (1)	0.9246 (7)	0.813 (2)	16.5 (7)
C12	0.2752 (4)	0.4144 (3)	0.0620 (6)	3.6 (2)
C13	0.4140 (4)	0.4092 (3)	0.1102 (6)	3.0 (2)
C14	0.4882 (4)	0.3447 (3)	0.0090 (6)	3.6 (2)
C15	0.6159 (4)	0.3557 (4)	0.0540 (7)	4.3 (2)
C16	0.6729 (4)	0.4304 (5)	0.2078 (7)	4.7 (2)
C17	0.6038 (4)	0.4926 (4)	0.3160 (7)	4.6 (2)
C18	0.4768 (4)	0.4833 (4)	0.2645 (6)	3.8 (2)

Table 2. Bond distances (Å) and bond angles (°) in C₁₈H₂₇N₃O₅Si

Si1—C8	1.877 (5)	N2—C12	1.482 (5)
Si1—C9	1.874 (8)	N3—C14	1.452 (6)
Si1—C10	1.79 (1)	C1—C2	1.505 (7)
Si1—C11	1.807 (9)	C2—C3	1.519 (6)
O1—C1	1.211 (5)	C2—C4	1.521 (7)
O2—C6	1.191 (5)	C3—C5	1.506 (7)
O3—C6	1.328 (5)	C7—C8	1.485 (7)
O3—C7	1.456 (6)	C12—C13	1.505 (5)
O4—N3	1.207 (5)	C13—C14	1.392 (6)
O5—N3	1.217 (5)	C13—C18	1.390 (6)
N1—N2	1.435 (4)	C14—C15	1.391 (6)
N1—C1	1.392 (6)	C15—C16	1.372 (7)
N1—C6	1.390 (6)	C16—C17	1.374 (7)
N2—C3	1.484 (5)	C17—C18	1.380 (6)
C8—Si1—C9	108.2 (3)	C3—C2—C4	119.7 (5)
C8—Si1—C10	109.2 (4)	N2—C3—C2	104.1 (4)
C8—Si1—C11	111.4 (3)	N2—C3—C5	109.4 (4)
C9—Si1—C10	109.4 (6)	C2—C3—C5	113.8 (4)
C9—Si1—C11	105.3 (5)	O2—C6—O3	126.0 (4)
C10—Si1—C11	113.2 (7)	O2—C6—N1	124.0 (5)
C6—O3—C7	116.4 (4)	O3—C6—N1	110.0 (4)
N2—N1—C1	112.5 (3)	O3—C7—C8	107.6 (4)
N2—N1—C6	120.9 (3)	Si1—C8—C7	118.0 (4)
C1—N1—C6	126.5 (4)	N2—C12—C13	110.2 (3)
N1—N2—C3	102.1 (3)	C12—C13—C14	127.3 (4)
N1—N2—C12	108.7 (3)	C12—C13—C18	117.1 (4)
C3—N2—C12	113.0 (3)	C14—C13—C18	115.3 (4)
O4—N3—O5	121.3 (5)	N3—C14—C13	121.2 (3)
O4—N3—C14	119.3 (5)	N3—C14—C15	116.0 (4)
O5—N3—C14	119.4 (5)	C13—C14—C15	122.8 (4)
O1—C1—N1	125.8 (4)	C14—C15—C16	119.3 (4)
O1—C1—C2	127.9 (5)	C15—C16—C17	119.9 (4)
N1—C1—C2	106.3 (4)	C16—C17—C18	119.7 (4)
C1—C2—C3	102.2 (4)	C13—C18—C17	122.9 (4)
C1—C2—C4	112.1 (4)		

C12—C13—C18 and C14—C13—C18 angles to 117.1 (4) and 115.3 (4)°, respectively.

Also associated with the *o*-nitro group in (4) is an N3—C14 bond length of 1.452 (6) Å. This value is similar to that observed in *o*-nitrobenzoic acid [1.478 (13) Å] but slightly shorter than that in *p*-nitrotoluene [1.528 (9) Å].

The remaining functionality in (4) comprises what is formally an *N*-amino-*N*-acylcarbamate (Fig. 1). In this subunit the carbonyl groups adopt a *Z,Z* conformation with C—O distances that are consistent with normal double bonding. The C1—N1 and C6—N1 bond distances of 1.392 (6) and 1.390 (6) Å, respectively, are similar to the corresponding C—N lengths found in imides (Hvoslef, Tracy & Nash, 1986), but are considerably longer than the C—N distances found in amides. Examination of the intramolecular bond angles associated with atom N1 suggests that it lies in a planar environment. The sum of the bond angles about atom N1 is 359.9°, and the O1—C1—N1—C6 and O2—C6—N1—C1 torsion angles are 6.7 (8) and 0.4 (8)°, respectively. These data, when considered with the shortened C—N bond distances noted above, imply a certain degree of delocalization of electron density from atom N1 into both carbonyl groups. The geometry around atom N2 appears tetrahedral, displaying the bond angles N1—N2—C3 102.1 (3), N1—N2—C12 108.7 (3) and C3—N2—C12 113.0 (3)°.

The N1—N2 bond distance of 1.435 (4) Å in the pyrazolidinone ring is comparable to the 1.449 (4) Å

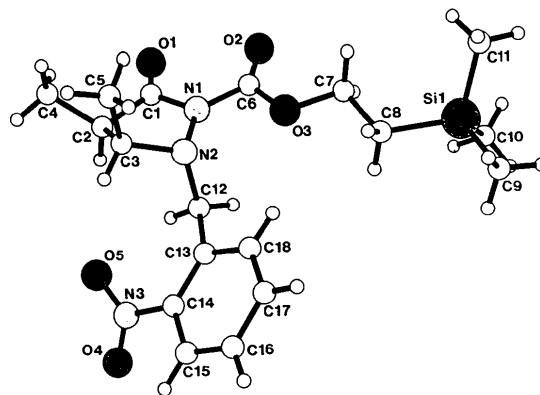
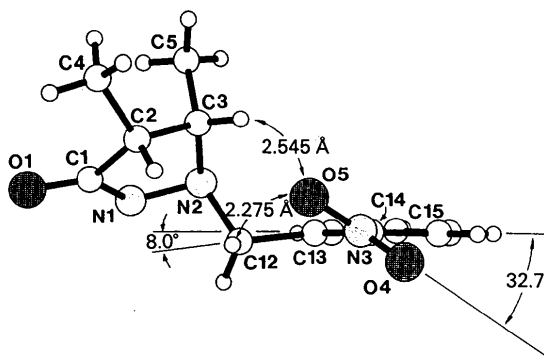


Fig. 1. Molecular drawing of (4) showing atom-numbering scheme.

Fig. 2. Partial structure of (4) showing the features associated with the *o*-nitrobenzyl group.

N—N single bond of hydrazine (Morino, Iijima & Murata, 1960). It is also in agreement with the N—N bond length of 1.443 (3) Å present in the 2-phenylpyrazolidin-3-one studied by Ege *et al.* (1983). In contrast, the N1—N2 bond length in (4) is slightly longer than the 1.396 (9) Å N—N bond distance in 1,2-diacetylhydrazine (Shintani, 1960) and longer still when compared with the N—N bond length of 1.346 (6) Å in tetraformyl hydrazine (Hinderer & Hess, 1974).

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Structures of Diels-Alder Reaction Adducts of Certain Propellanes with 4-Phenyl-1,2,4-triazoline-3,5-dione

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Abstract. 1a,8b-Dihydro-5-phenyl-2*H*,8*H*-2,8-etheno-1b,8a-(methanoxymethano)-4*H*-oxireno[3,4]cyclobuta[1,2-*d*][1,2,4]triazolo[1,2-*A*]pyridazine-4,6(5*H*)-dione: isomer (1), C₁₈H₁₅N₃O₄, *M_r* = 337.33, orthorhombic, *P*2₁2₁2₁, *a* = 23.866 (11), *b* = 9.571 (5), *c* = 6.686 (3) Å, *V* = 1527.22 Å³, *Z* = 4, *D_x* = 1.467 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.991 cm⁻¹, *F*(000) = 704, *R* = 0.059 for 1560 reflections; isomer (2), C₁₈H₁₅N₃O₄, *M_r* = 337.33, orthorhombic, *P*2₁2₁2₁, *a* = 24.104 (12), *b* = 9.774 (5), *c* = 6.463 (3) Å, *V* = 1522.63 Å³, *Z* = 4, *D_x* = 1.461 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.994 cm⁻¹, *F*(000) = 704, *R* = 0.095 for 866 reflections. 1a,8b-Dihydro-1a,8b-dimethyl-5-phenyl-2*H*,8*H*-2,8-etheno-1b,8a-(methanoxymethano)-4*H*-oxireno[3,4]cyclobuta[1,2-*d*][1,2,4]triazolo[1,2-*a*]pyridazine-4,6(5*H*)-dione: isomer (3), C₂₀H₁₉N₃O₄, *M_r* = 365.39, orthorhombic, *P*2₁2₁2₁, *a* = 13.096 (6), *b* =

12.653 (6), *c* = 10.696 (5) Å, *V* = 1772.36 Å³, *Z* = 4, *D_x* = 1.369 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.908 cm⁻¹, *F*(000) = 768, *R* = 0.066 for 1758 reflections; isomer (4), C₂₀H₁₉N₃O₄, *M_r* = 365.39, monoclinic, *P*2₁/*c*, *a* = 26.724 (13), *b* = 11.985 (6), *c* = 11.453 (6) Å, β = 99.96 (2)°, *V* = 3612.96 Å³, *Z* = 8, *D_x* = 1.343 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.891 cm⁻¹, *F*(000) = 1536, *R* = 0.036 for 2649 reflections. 13-Hydroxy-13-methyl-14-methylene-2-phenyl-6*H*,9*H*-5a,8a-ethano-5,9-etheno-1*H*,5*H*,8*H*-furo[3,4-*d*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (5), C₂₀H₁₉N₃O₄, *M_r* = 365.39, monoclinic, *P*2₁/*c*, *a* = 13.474 (7), *b* = 11.422 (6), *c* = 11.534 (6) Å, β = 97.73 (2)°, *V* = 1758.95 Å³, *Z* = 4, *D_x* = 1.379 g cm⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.915 cm⁻¹, *F*(000) = 768, *R* = 0.070 for 2095 reflections. Crystal structures of the Diels-Alder adducts of 4-phenyl-1,2,4-triazoline-3,5-dione with various