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Structure of 6-(*tert*-Butylimino)-4,4,5,5-tetracyano-3-(1-phenylethylidene)-1-(trimethylsilyl)cyclohex-1-ene

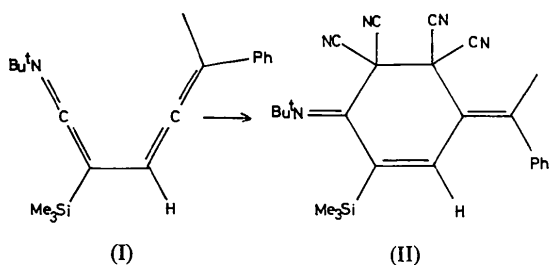
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Abstract. 6-(*tert*-Butylimino)-3-(1-phenylethylidene)-1-(trimethylsilyl)-1-cyclohexene-4,4,5,5-tetracarbonitrile, $C_{25}H_{27}N_5Si$, $M_r = 425.61$, orthorhombic, *Pbca*, $a = 16.454$ (3), $b = 17.353$ (3), $c = 17.674$ (1) Å, $V = 5046.4$ Å³, $Z = 8$, $D_m = 1.11$ (2), $D_x = 1.120$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.83$ cm⁻¹, $F(000) = 1808$, ambient temperature, $R = 0.063$ for 2891 observed [$F > 2\sigma(F)$] reflections. The heavy substitution on the cyclohexene ring distorts the imino group out of conjugation with the ring double bond.

Introduction. We have been investigating the use of titanocene vinylidene complexes generated *in situ* from the 1-dimethylalumino-1-bis(cyclopentadienyl)-chlorotitanoalkenes for the carbometallation of unactivated alkenes and alkynes (Dennehy & Whitby, 1990). The intramolecular addition of these reagents to alkynes affords titanocyclobutenes which undergo an unusual reaction with 'BuNC to give unstable allenyl ketenimines (Dennehy & Whitby, 1992). Compound (I) was isolated as the stable tetracyanoethylene adduct (II) which gave crystals suitable for X-ray examination, and the structure is reported herein.



Experimental. Colourless crystal (0.25 × 0.37 × 0.20 mm), from 40–60 petroleum ether–diethyl ether, mounted in glass capillary. Preliminary photographic X-ray examination. Density by flotation (CCl₄–hexane). Enraf–Nonius FAST area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation and a crystal to detector distance of 40 mm [refined to 40.38 (2) mm]. Unit-cell parameters and orientation matrix from 250 reflections. 19 281 reflections measured (one hemisphere, $2\theta_{\text{max}} = 53.5^\circ$) and processed using the *ABSURD* software package, Lorentz and polarization corrections, no absorption or decay correction (Danopoulos, Wilkinson, Hussain-Bates & Hursthouse, 1991). Space group *Pbca* (No. 61) from systematic absences, 4559 unique reflections ($R_{\text{int}} = 0.065$), 2891 reflections with $F > 2\sigma(F)$ and $2\theta < 50^\circ$ used (h 0–18, k 0–19, l 0–20 after transformation). Structure solution by *SHELXS86* (Sheldrick, 1986) and refined by *SHELX76* (Sheldrick, 1976) using full-matrix least squares on F . Nearly all of the H atoms appeared on a difference electron-density synthesis ($R = 0.102$) but with disorder in the trimethylsilyl and *tert*-butyl residues. Final $R = 0.063$, $wR = 0.067$, 303 parameters, anisotropic (C, N, Si) and isotropic (H) atoms, H atoms in calculated positions [$C-H = 0.95$ Å], $w = [\sigma^2(F) + 0.00015F^2]^{-1}$, $S = 0.69$. Maximum Δ/σ in final cycle 0.1, $\Delta\rho$ for final model < 0.40 and > -0.31 e Å⁻³. Neutral-atom scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) (Si only) and *SHELX76*. Fig. 1 was drawn using *ORTEPII* (Johnson, 1976) and all calculations were carried out on an IBM 3090 computer.

Discussion. Atomic coordinates for non-H atoms are listed in Table 1 and bond lengths and angles appear

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in Table 2.* The structure consists of discrete molecules (Fig. 1) and is in accord with that proposed in (II). The bond lengths are unexceptional and the feature of interest lies in the conformation imposed by the large substituents on the cyclohexene ring. Inspection of the torsion angles of the cyclohexene reveals approximate twofold symmetry and a half-chair conformation (Ladd & Palmer, 1985). This axis passes through the midpoints of C(1)—C(6) and C(3)—C(4) and, as expected, the torsion angle C(4)—C(5)—C(6)—C(1) is close to zero. The trimethylsilyl, *tert*-butyl residue on N(5) and the cyanide groups on contiguous carbon atoms pose severe steric clashes. Since twisting the C=N bond is energetically very unfavourable, the whole unit bends with loss of conjugation with the double bond [C(6)—C(5)—C(4)—N(5) = 120°]. Introducing N(5) and Si(1) into geometrically idealized positions and comparison of these angles with the experimental values show that ring torsion angles have changed by some 10° to minimize repulsions. The phenyl ring is twisted with consequent loss of conjugation with the double bond [C(1)=C(7)] probably as a result of the vinyl proton. The structure is fully consistent with the proposed structure of the allenyl ketenamine (I).

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* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions and complete geometric details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54934 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0095]

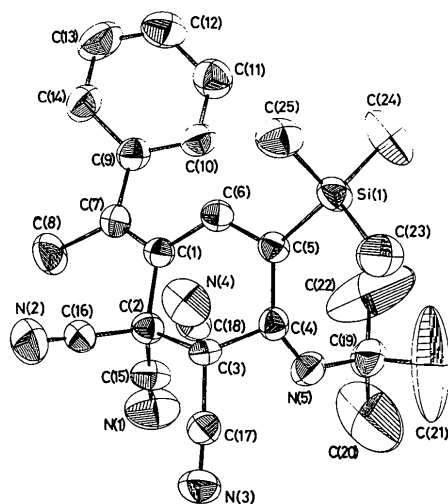


Fig. 1. Structure of a discrete molecule in $C_{25}H_{27}N_5Si$ showing the atom-numbering scheme. H atoms are omitted for clarity and the ellipsoids are drawn at the 50% probability level.

Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Si(1)	0.71723 (8)	0.12391 (6)	0.28210 (6)	50.2 (7)
N(1)	0.6589 (3)	0.4335 (2)	0.0675 (2)	82.0 (31)
N(2)	0.4283 (3)	0.3362 (2)	0.1261 (2)	80.5 (31)
N(3)	0.6074 (2)	0.2481 (2)	-0.0333 (2)	65.5 (27)
N(4)	0.5181 (2)	0.1334 (2)	0.1578 (2)	75.4 (29)
N(5)	0.7565 (2)	0.2452 (2)	0.1008 (2)	49.4 (21)
C(1)	0.6077 (2)	0.3363 (2)	0.2305 (2)	37.9 (22)
C(2)	0.5852 (2)	0.3263 (2)	0.1462 (2)	39.3 (23)
C(3)	0.6138 (2)	0.2449 (2)	0.1146 (2)	37.6 (22)
C(4)	0.7008 (2)	0.2328 (2)	0.1477 (2)	38.6 (23)
C(5)	0.6923 (2)	0.2173 (2)	0.2302 (2)	38.7 (22)
C(6)	0.6471 (2)	0.2702 (2)	0.2668 (2)	39.5 (22)
C(7)	0.5897 (2)	0.4019 (2)	0.2690 (2)	41.2 (23)
C(8)	0.5397 (3)	0.4671 (2)	0.2364 (2)	63.3 (30)
C(9)	0.6234 (2)	0.4156 (2)	0.3454 (2)	42.8 (24)
C(10)	0.7043 (2)	0.4023 (2)	0.3622 (2)	48.5 (26)
C(11)	0.7355 (3)	0.4197 (3)	0.4324 (2)	61.0 (31)
C(12)	0.6867 (3)	0.4488 (3)	0.4873 (2)	67.2 (33)
C(13)	0.6060 (3)	0.4620 (3)	0.4726 (2)	74.1 (36)
C(14)	0.5744 (3)	0.4464 (2)	0.4021 (2)	57.9 (29)
C(15)	0.6271 (3)	0.3865 (2)	0.1000 (2)	49.8 (27)
C(16)	0.4969 (3)	0.3336 (2)	0.1343 (2)	48.6 (27)
C(17)	0.6127 (2)	0.2463 (2)	0.0306 (2)	45.6 (25)
C(18)	0.5589 (2)	0.1829 (2)	0.1397 (2)	46.2 (25)
C(19)	0.8442 (3)	0.2526 (3)	0.1171 (2)	62.0 (31)
C(20)	0.8774 (4)	0.3022 (6)	0.0578 (5)	199.9 (89)
C(21)	0.8837 (5)	0.1790 (5)	0.1061 (7)	238.2 (108)
C(22)	0.8648 (4)	0.2789 (8)	0.1905 (4)	255.6 (108)
C(23)	0.7323 (4)	0.0466 (3)	0.2102 (2)	86.5 (40)
C(24)	0.8027 (3)	0.1379 (4)	0.3482 (3)	97.7 (45)
C(25)	0.6257 (3)	0.0977 (3)	0.3383 (2)	72.9 (35)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

C(1)—C(2)	1.544 (4)	C(4)—C(5)	1.489 (4)
C(2)—C(3)	1.591 (5)	C(5)—C(6)	1.345 (5)
C(3)—C(4)	1.561 (5)	C(6)—C(1)	1.466 (5)
C(1)—C(7)	1.359 (4)	C(7)—C(8)	1.513 (5)
C(7)—C(9)	1.480 (4)	C(5)—Si(1)	1.907 (3)
C(2)—C(15)	1.495 (5)	C(15)—N(1)	1.126 (5)
C(2)—C(16)	1.473 (5)	C(16)—N(2)	1.139 (5)
C(3)—C(17)	1.484 (5)	C(17)—N(3)	1.134 (4)
C(3)—C(18)	1.475 (5)	C(18)—N(4)	1.135 (5)
C(4)—N(5)	1.255 (4)	N(5)—C(19)	1.476 (5)
C(2)—C(15)—N(1)	177.4 (4)	C(3)—C(17)—N(3)	176.3 (4)
C(2)—C(16)—N(2)	177.2 (5)	C(3)—C(18)—N(4)	177.7 (4)
C(3)—C(4)—N(5)	113.5 (3)	C(4)—N(5)—C(19)	126.9 (3)
C(5)—C(4)—N(5)	138.3 (3)		

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