

The insensitivity of the ring geometry to substituent effects raises the question of whether the compound $(\text{Bu}_2\text{Si.NBu})_2$ is sterically too crowded to be stable, or whether the steric bulk of the substituents has simply prevented a synthesis by the direct methods so far attempted. In this context, we note that the cyclotrisiloxane $(\text{Bu}_2\text{SiO})_3$ cannot be prepared by elimination of water from $\text{Bu}_2\text{Si}(\text{OH})_2$ (a reaction which normally occurs very readily for such compounds) and necessitates a multi-step synthetic route (Sommer & Tyler, 1954; Klingebiel, 1981). We have performed simple calculations in which the Pr groups of $(\text{Pr}_2\text{Si.NBu})_2$ are replaced by Bu groups with $\text{C}-\text{C} = 1.53 \text{ \AA}$ and ideal tetrahedral angles at the central C atom, while retaining the $(\text{C}_2\text{Si.NBu})_2$ part of the molecule unchanged. We find several $\text{C}\cdots\text{C}$ distances under 3 \AA for methyl C atoms in different Bu groups. Concerted rotation about the Si-C bonds reduces the steric interference between Bu groups attached to each Si atom [as is observed in $(\text{Bu}_2\text{SiO})_3$, where all the Bu groups fit snugly together (Clegg, 1982; Puff, Franken, Schuh & Schwab, 1983)], but the short contacts between Bu groups attached to Si and N are not relieved by such Si-C or N-C rotations. In $(\text{Pr}_2\text{Si.NBu})_2$ the substituents are oriented to avoid all such short contacts (Fig. 1), and the shortest $\text{C}\cdots\text{C}$ between methyl groups on different Bu substituents is $2.99 (1) \text{ \AA}$. We conclude that $(\text{Bu}_2\text{Si.NBu})_2$ is probably too crowded to be stable, at least with a planar central Si_2N_2 ring of the form always observed so far for cyclodisilazanes. In contrast, $(\text{Bu}_2\text{Si.PBu})_2$ has been prepared and structurally characterized (Clegg, Haase, Klingebiel & Sheldrick, 1983); in this molecule,

however, the mean Si-P bond length is 2.259 \AA , so steric crowding is much smaller.

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Structure of 2-(1,2-Dihydro-1-methyl-2-pyridylidene)-3-(4-ethoxyphenyl)-3-oxopropanenitrile, $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2^*$

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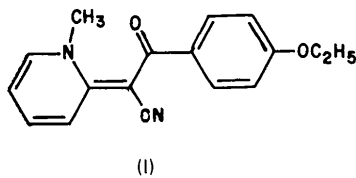
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Abstract. $M_r = 280.2$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.199 (2)$, $b = 8.473 (1)$, $c = 12.360 (1) \text{ \AA}$, $\alpha = 101.73 (1)$, $\beta = 94.37 (2)$, $\gamma = 100.10 (2)^\circ$, $V = 721.9 \text{ \AA}^3$, $D_m(\text{floatation}) = 1.24$, $D_x = 1.25 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 7.18 \text{ mm}^{-1}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $F(000) = 496.0$, $T = 293 \text{ K}$, $R = 0.052$ for 1082 observed reflections. The molecular structure obtained from the present study is in agreement with that obtained

from spectral data. The $\text{C}=\text{C}$ distance is $1.438 (6) \text{ \AA}$, appreciably longer than normal. The steric and electronic effects result in rotation about the $\text{C}=\text{C}$ bond, the rotation angle being $40.7 (6)^\circ$.

Introduction. The title compound (I) was obtained during an attempt to prepare substituted 2-azabarelenones by cycloaddition reactions between 1-methyl-2(1H)-pyridone and 3-substituted propyne-nitrile (Yadla & Madhusudhana Rao, 1984). The

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crystal structure analysis was undertaken to study the steric and electronic influences on the polarized ethylene moiety.

Experimental. Crystal approx. 0.15 × 0.25 × 0.25 mm. Nonius CAD-4F-11M diffractometer, graphite-monochromated Mo K α radiation, $\omega/2\theta$ scan mode, scan speed 1° min⁻¹, $\theta \leq 24^\circ$; h 0 to 8, k -9 to 9, l -14 to 13. 2442 reflections collected, 1082 judged significant ($|F_o| > 3\sigma|F_c|$). No correction for absorption. Structure solved by direct methods, program MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement of scale factors, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0.052$ and $R_w = 0.046$; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = (1.5 + 1.0|F_o| + 0.033|F_o|^2)^{-1}$. Max. (Δ/σ) = 0.1. Final $\Delta\rho$ excursions $< |0.3| e \text{ \AA}^{-3}$. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). LALS (Gantzel, Sparks & Trueblood, 1961) for refinement.

Discussion. The atomic parameters with their e.s.d.'s and equivalent isotropic temperature factors are given in Table 1.* Bond lengths and bond angles involving the non-hydrogen atoms are given in Table 2. Fig. 1 gives a perspective view of the molecule along with the numbering of the atoms.

The C-C bond length of 1.438 (6) Å differs significantly from the value for ethylene [1.336 (2) Å] (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965). The longer C=C distance suggests that the methylpyridine ring is a good electron-releasing group. Owing to the steric bulk of the *N*-methylpyridine moiety and also that of the ethoxyphenyl substituent, the C=C bond is twisted. The twist angle defined as the angle between the plane through N(1), C(4), C(3) and the plane through C(7), C(6), C(16) is 40.7 (6)°. The twist about C=C can also be described in terms of three

Table 1. Final positional parameters ($\times 10^4$) and isotropic thermal parameters, with e.s.d.'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
O(1)	2164 (4)	7290 (4)	3517 (3)	4.1 (2)
O(2)	3951 (5)	1986 (4)	-412 (3)	4.6 (2)
N(1)	-1682 (5)	8135 (4)	3878 (3)	3.2 (2)
N(2)	-2205 (6)	2442 (5)	3190 (4)	5.3 (2)
C(1)	-3259 (7)	8869 (6)	5465 (4)	4.1 (2)
C(2)	-3383 (7)	7280 (6)	5645 (4)	4.2 (2)
C(3)	-2570 (6)	6176 (5)	4952 (4)	3.7 (2)
C(4)	-1644 (6)	6612 (5)	4069 (3)	3.1 (2)
C(5)	-2439 (7)	9259 (6)	4585 (4)	4.1 (2)
C(6)	-734 (6)	5486 (5)	3363 (3)	3.1 (2)
C(7)	1139 (6)	5965 (5)	3049 (3)	3.5 (2)
C(8)	1858 (6)	4864 (5)	2158 (3)	3.1 (2)
C(9)	707 (6)	3785 (7)	1282 (4)	4.6 (2)
C(10)	1430 (7)	2849 (7)	427 (4)	4.9 (2)
C(11)	3382 (7)	2976 (5)	456 (4)	3.7 (2)
C(12)	4564 (6)	4061 (5)	1318 (4)	3.7 (2)
C(13)	3805 (6)	4986 (5)	2156 (3)	3.5 (2)
C(14)	5961 (6)	1987 (6)	-418 (4)	4.1 (2)
C(15)	6176 (7)	819 (6)	-1469 (4)	4.9 (2)
C(16)	-1512 (6)	3794 (5)	3253 (4)	3.7 (2)
C(17)	-1067 (7)	8607 (6)	2864 (4)	4.2 (2)

Table 2. Intramolecular bond lengths (Å) and angles (°), with e.s.d.'s in parentheses

O(1)-C(7)	1.233 (5)	O(2)-C(11)	1.358 (6)
O(2)-C(14)	1.448 (6)	N(1)-C(4)	1.363 (5)
N(1)-C(5)	1.372 (6)	N(1)-C(17)	1.467 (6)
N(2)-C(16)	1.151 (6)	C(1)-C(2)	1.398 (7)
C(1)-C(5)	1.348 (7)	C(2)-C(3)	1.376 (7)
C(3)-C(4)	1.400 (6)	C(4)-C(6)	1.438 (6)
C(6)-C(7)	1.444 (6)	C(6)-C(16)	1.419 (6)
C(7)-C(8)	1.480 (6)	C(8)-C(9)	1.374 (6)
C(8)-C(13)	1.387 (6)	C(9)-C(10)	1.380 (7)
C(10)-C(11)	1.388 (7)	C(11)-C(12)	1.376 (6)
C(12)-C(13)	1.375 (6)	C(14)-C(15)	1.501 (7)
C(11)-O(2)-C(14)	118.2 (4)	C(7)-C(8)-C(13)	118.9 (4)
C(4)-N(1)-C(17)	121.8 (6)	C(8)-C(9)-C(10)	122.2 (5)
C(2)-C(1)-C(5)	119.4 (5)	O(2)-C(11)-C(10)	114.8 (4)
C(2)-C(3)-C(4)	121.2 (4)	C(10)-C(11)-C(12)	119.6 (4)
N(1)-C(4)-C(6)	120.8 (4)	C(8)-C(13)-C(12)	121.7 (4)
N(1)-C(5)-C(1)	121.1 (4)	N(2)-C(16)-C(6)	177.0 (5)
C(4)-C(6)-C(16)	115.5 (4)	C(4)-N(1)-C(5)	121.4 (4)
O(1)-C(7)-C(6)	120.8 (4)	C(5)-N(1)-C(17)	116.6 (4)
C(6)-C(7)-C(8)	120.2 (4)	C(1)-C(2)-C(3)	119.0 (4)
N(1)-C(4)-C(3)	117.5 (4)	C(3)-C(4)-C(6)	121.7 (4)
C(4)-C(6)-C(7)	122.6 (4)	C(7)-C(6)-C(16)	119.5 (4)
O(1)-C(7)-C(8)	119.0 (4)	C(7)-C(8)-C(9)	123.6 (4)
C(9)-C(8)-C(13)	117.3 (4)	C(9)-C(10)-C(11)	119.2 (5)
O(2)-C(11)-C(12)	125.6 (4)	C(11)-C(12)-C(13)	119.9 (4)
O(2)-C(14)-C(15)	106.8 (4)		

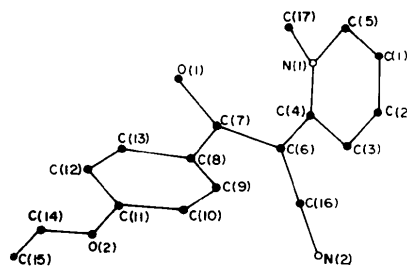


Fig. 1. A perspective view of the molecule. The numbering scheme is an arbitrary crystallographic choice.

* Lists of structure factors, anisotropic thermal parameters H-atom parameters and some important torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39172 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

dihedral angles, $\chi[C(4)]$, $\chi[C(6)]$ and $\tau[C(4)=C(6)]$, similar to that for the amide group (Winkler & Dunitz, 1971); these are $\chi[C(4)] = 2.0$ (5), $\chi[C(6)] = 18.1$ (6), $\tau[C(4)=C(6)] = 15.6$ (5) $^\circ$ respectively. A similar analysis about N(1) and C(4) gives $\chi[N(1)] = 5.6$ (6), $\chi[C(4)] = 2.0$ (6) and $\tau[C(4)-N(1)] = 7.2$ (6) $^\circ$, showing the nonplanar characteristics about the C-N bond. There are significant changes in the bond lengths due to conjugation. The $C_{sp^2}-C_{sp}$ bond length of 1.419 (6) Å differs significantly from the values reported in ethylenetetra-carbonitrile [1.437 (2) Å (Little, Pautler & Coppens, 1971)]. The N(1)-C(4) distance [1.363 (5) Å] is significantly shorter than the corresponding N-C distance in *N,N',N'',N'''*-tetraphenyl-2,2'-bi(imidazolidinylidene) [1.403 (3) Å (Hitchcock, 1979)] but compares with those observed in (1,3-dimethyl-2-imidazolidinylidene)malononitrile and (1,3-dimethyl-2-perhydropyrimidinylidene)malononitrile [1.335 (5)-1.352 (2) Å (Adhikesavalu & Venkatesan, 1982)]. The two six-membered rings are inclined at an angle of 81.3 (6) $^\circ$. The crystal packing is solely through van der Waals interactions.

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Structure of 2-Chloro-5-methyl-6-phenyl-3-(*p*-tolyl)perhydro-1,3,2λ⁵-oxazaphosphorine 2-Oxide, C₁₇H₁₉ClNO₂P*

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Abstract. $M_r = 335.8$, monoclinic, $P2_1/a$, $Z = 4$, $a = 12.253$ (2), $b = 11.650$ (2), $c = 12.646$ (2) Å, $\beta = 109.05$ (2) $^\circ$, $V = 1706.3$ Å³, D_m (floatation) = 1.25, $D_x = 1.31$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.51$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $F(000) = 704.0$, $T = 293$ K, $R = 0.070$ for 942 observed reflections. The 1,3,2-oxazaphosphorine ring adopts a chair conformation. The exocyclic O and Cl connected to P are in equatorial and axial positions respectively. The bond lengths and angles are normal. The packing of the molecules in the unit cell involves van der Waals contacts.

Introduction. As part of a programme of X-ray studies on the structure and conformation of oxazaphosphorine ring systems, which are known to be clinically useful anticancer drugs, the title compound was prepared (Sahasrabudhe & Tilak, 1983). Several

recent studies have shown that the 1,3,2-oxazaphosphorine ring undergoes conformational changes due to steric and electronic influences on P (Bajwa, Bentrude, Pantaleo, Newton & Hargis, 1979; Gorenstein & Rowell, 1979; Gorenstein, Rowell & Findlay, 1980; Maryanoff, Hutchins & Maryanoff, 1979) and to the substituents on ring N (Chandrasekharan & Bentrude, 1980; Bajwa, Chandrasekharan, Hargis, Sopchik, Blatter & Bentrude, 1982).

Experimental. Crystal (orange needle from alcohol solution) approximately 0.15 × 0.25 × 0.38 mm. Lattice parameters from 21 reflections ($12^\circ < 2\theta < 36^\circ$). Nonius CAD-4F-11M single-crystal X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1 $^\circ$ min⁻¹, $\theta \leq 24^\circ$, h 0 to 10, k 0 to 13, l -14 to 12. 2819 reflections collected, 942 significant ($|F_o| \geq 3\sigma|F_o|$). No correction for absorption. Structure solved by direct methods,

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