The Sb—C bond lengths [2·181–2·201 (8) Å] show no significant variation dependent upon the mesityl ring orientation. The sum of the angles at Sb1 and Sb2 is 299·9 and 298·2° respectively, which is larger than the values observed for tetraphenyldistibane in which the sum of the angles at the Sb atoms was 284·7 (von Deuten & Rehder, 1980) and 285·2° (Becker, Freudenblum & Witthauer, 1982).

Fig. 2 displays the unit-cell packing for tetramesityldistibane. Thermochromic effects in distibane complexes have been seen to occur (*e.g.* Becker, Freudenblum & Witthauer, 1982; Ashe, Ludwig, Oleksyszyn & Huffman, 1984), where the Sb atoms are arranged in collinear chains with the Sb–Sb separations well below the van der Waals separation of 4·4 Å. For tetramesityldistibane the Sb2—Sb2 vectors are not collinear with neighbouring molecules, with the closest intramolecular contact between Sb atoms being 6·40 Å. This far exceeds the van der Waals separation and precludes the possibility of extended bonding between the Sb atoms of neighbouring molecules.

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Structure of 5-(2,2,6,6-Tetramethyl-1-oxyl-1,2,5,6-tetrahydropyridin-4-yl)penta-2,4-diyn-1-ol

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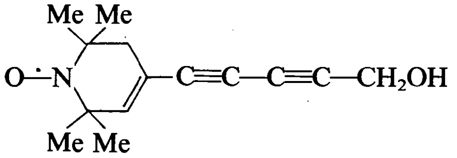
Abstract. $C_{14}H_{18}NO_2$, $M_r = 232$, monoclinic, $P2_1/n$, $a = 5{\cdot}760\,(1)$, $b = 22{\cdot}064\,(4)$, $c = 10{\cdot}520\,(1)$ Å, $\beta = 103{\cdot}98\,(1)^\circ$, $V = 1297{\cdot}3\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}86$ cm^{-1}, $F(000) = 125$, $T = 150$ K, $R = 0{\cdot}058$ for 1386 reflections. The six-membered heterocycle has a distorted half-chair conformation. The N atom of the paramagnetic centre is displaced from the plane of the three bonded atoms by 0·120 (3) Å. The N—O distance is 1·279 (4) Å, the N—C distances are 1·491 and 1·482 (4) Å. The molecules are linked by O—H···O 'head-to-tail' hydrogen bonds into infinite chains along [10$\bar{1}$] which in their turn form layers parallel to (010). Packing of the molecules in the crystal satisfies the conditions for solid state polymerization of diacetylenes; however, due to the fixation of molecular positions in the crystal by hydrogen bonds this particular compound is quite stable relative to the solid state polymerization.

Introduction. An X-ray structural study of 5-(2,2,6,6-tetramethyl-1-oxyl-1,2,5,6-tetrahydropyridin-4-yl)penta-2,4-diyn-1-ol (I), prepared by the conventional technique of the cross-coupling of monosubstituted acetylenes (Chodkiewich, 1957), has been carried out and the possibility of its solid state polymerization is discussed.



(I)

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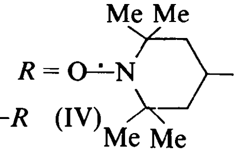
The structures of monosubstituted acetylene (II) and disubstituted diacetylenes [(III)–(V)] with the stable radicals in the side chains have previously been studied (Cygler, 1988; Shklover, Zamaev, Ovchinnikov, Struchkov, Medvedeva, Korshak, Specktor & Ovchinnikov, 1987; Miller, Glatzhofer, Calabrese & Epstein, 1988; Shklover, Zamaev, Ovchinnikov, Struchkov, Bubnov, Gursky, Shapiro, Lazareva, Vinogradov, Schegolichin & Ovchinnikov, 1987; Shklover, Zamaev, Struchkov, Medvedeva, Korshak, Ovchinnikov & Specktor, 1987).

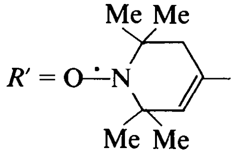
$R—C≡CH$ (II)

$R—C≡C—C≡C—R$ (III)

$R—CH_2—C≡C—C≡C—CH_2—R$ (IV)



$R'—C≡C—C≡C—R'$ (V)



Although solid state polymerization is likely to occur in the crystals of the α-phase of (III) (Shklover, Zamaev, Struchkov, Medvedeva, Korshak, Ovchinnikov & Specktor 1987), the molecular packing in crystals (II)–(V) does not satisfy the conditions for topochemical polymerization (Baughman, 1974). The study of the solid state polymerization of diacetylenes with stable radicals in the side chains is of interest in connection with the more general problem of the preparation of organic ferromagnetics by this approach (Korshak, Ovchinnikov, Shapiro, Medvedeva & Specktor, 1986). In the present work the crystal structure of the non-symmetrically substituted diacetylene with the stable nitroxyl radical as one of the substituents has been studied first.

Experimental. Crystal size 0·2 × 0·3 × 0·4 mm. Unit-cell parameters were from 24 reflections with $22 \leq 2\theta \leq 24°$. Automated Syntex $P2_1$ four-circle diffractometer, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 60°$ ($-8 \leq h \leq 8$, $0 \leq k \leq 32$, $0 \leq l \leq 15$). No noticeable changes in the intensities of two standard reflections (200 and 080), measured after every 98 reflections. Corrections for absorption and secondary extinction were not applied. Structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least-squares refinement with anisotropic thermal parameters for non-H atoms using 1386 unique reflections with $I > 3\sigma(I)$, $R_{int} \sim 4\%$ for 80 equivalent reflections. 410 unobserved reflections. Function $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + |0{\cdot}0125F_o|^2]^{-1}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms located from difference synthesis and refined isotropically. Final $R = 0{\cdot}058$, $wR = 0{\cdot}044$, $S = 2{\cdot}891$, $(\Delta/\sigma)_{max} = 0{\cdot}5$. Max. and min. peak heights in final difference Fourier synthesis $\pm 0{\cdot}5$ e Å^{-3}. All calculations carried out with an Eclipse S/200 computer using *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).*

Discussion. The geometry of molecule (I) is shown in Fig. 1. Atomic coordinates are given in Table 1. The six-membered piperidyl heterocycle has a sofa conformation, the C(8) atom being displaced by 0·546 (3) Å from the fragment, planar within 0·02 Å, formed by five other atoms of the ring. The analogous heterocycle of molecule (V) has a distorted boat conformation. The C(6)—C(10) distance of 1·337 (5) Å indicates the localized double bond. No distinct features suggesting π-interaction of this double bond either with the paramagnetic or with the diacetylene fragment have been observed. Indeed the geometry of the N–O paramagnetic fragment [with displacement of the N atom from the plane of the three bonded atoms equal to 0·120 (3) Å, the bond lengths N—O 1·279 (4), N—C 1·491 (4) and 1·482 (4) Å] is close to that observed in molecules (III)–(V). The bond lengths in the diacetylene fragment are unexceptional.

The packing of molecules in crystal (I) is of special interest. The strong hydrogen bonds O(1)—H[O(1)]···O(2′) ($x - 1, y, z + 1$), {O(1)···O(2′) 2·724 (4), H[O(1)]···O(2′) 1·866 (4), O(1)—H[O(1)] 0·87 (1) Å, O(1)H[O(1)]O(2′) 168·2 (2)°} link molecules (I) in the 'head-to-tail' fashion, thus forming infinite chains along [10$\bar{1}$] (Fig. 2). In their turn the chains are arranged into layers parallel to (010). In

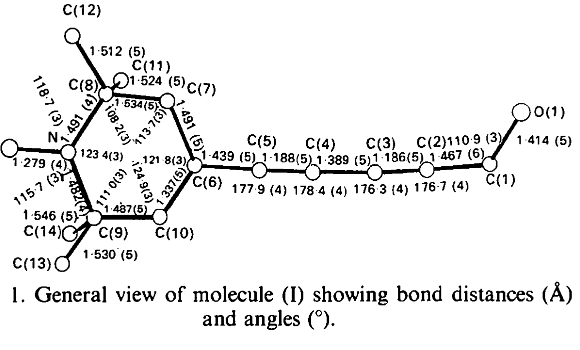


Fig. 1. General view of molecule (I) showing bond distances (Å) and angles (°).

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* Tables of structure factors, anisotropic thermal parameters, and bond lengths and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52405 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates* (× 10^4) *and equivalent isotropic thermal parameters of non*-H *atoms, and coordinates* (× 10^3) *and isotropic thermal parameters of* H *atoms*

	x	y	z	B_{eq}/B_{iso} (Å^2)
O(1)	1629 (5)	8146 (1)	9398 (2)	3·63 (9)
O(2)	11734 (4)	8806 (1)	1601 (2)	2·84 (7)
N	10318 (5)	8799 (3)	2369 (3)	2·02 (8)
C(1)	755 (7)	8615 (2)	8491 (4)	3·8 (1)
C(2)	2365 (7)	8719 (2)	7625 (4)	2·6 (1)
C(3)	3615 (6)	8778 (2)	6888 (3)	2·35 (9)
C(4)	5002 (6)	8817 (2)	5979 (3)	2·31 (9)
C(5)	6165 (6)	8837 (2)	5190 (3)	2·37 (9)
C(6)	7570 (6)	8837 (2)	4229 (3)	2·09 (9)
C(7)	8877 (7)	8269 (2)	4076 (4)	3·0 (1)
C(8)	9430 (6)	8204 (2)	2728 (3)	2·06 (9)
C(9)	9183 (6)	9386 (2)	2542 (3)	1·93 (9)
C(10)	7734 (7)	9335 (2)	3531 (4)	3·0 (1)
C(11)	7209 (7)	8027 (2)	1680 (4)	3·5 (1)
C(12)	11391 (6)	7737 (2)	2840 (4)	3·1 (1)
C(13)	11185 (6)	9851 (2)	2990 (4)	3·2 (1)
C(14)	7526 (7)	9579 (2)	1218 (4)	3·6 (1)
H(O1)	165 (6)	831 (2)	1015 (2)	6 (1)
H(1·1)	−117 (6)	854 (2)	785 (4)	6 (1)
H(1·2)	56 (6)	896 (2)	890 (3)	4·2 (9)
H(7·1)	1075 (8)	832 (2)	481 (5)	10 (2)
H(7·2)	775 (5)	794 (1)	414 (3)	3·1 (8)
H(10·1)	683 (5)	974 (1)	355 (3)	2·3 (7)
H(11·1)	667 (6)	764 (6)	175 (3)	4·4 (9)
H(11·2)	558 (6)	833 (2)	172 (4)	6 (1)
H(11·3)	754 (5)	803 (1)	82 (3)	3·3 (8)
H(12·1)	1304 (6)	790 (2)	342 (3)	4·4 (9)
H(12·2)	1200 (6)	767 (1)	206 (3)	4·4 (9)
H(12·3)	1093 (5)	737 (1)	323 (3)	3·1 (3)
H(13·1)	1186 (6)	987 (2)	218 (3)	5·2 (9)
H(13·2)	1042 (6)	1021 (1)	306 (3)	3·9 (9)
H(13·3)	1249 (5)	967 (1)	391 (3)	4·4 (9)
H(14·1)	870 (7)	958 (2)	67 (4)	6 (1)
H(14·2)	590 (8)	925 (2)	112 (5)	10 (1)
H(14·3)	677 (6)	992 (2)	134 (4)	6 (1)

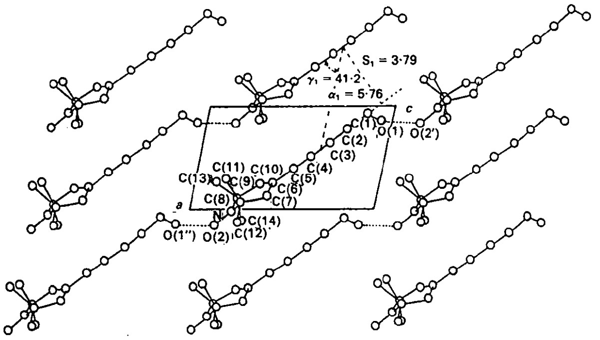
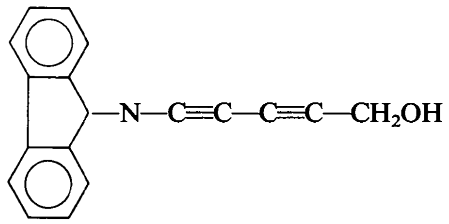


Fig. 2. The (010) projection of the crystal structure of (I) (molecules of only one layer are shown). The hydrogen bonds O(1)—H[O(1)]···O(2′) are shown by dotted lines. The values of the parameters S_1, α_1 (Å) and γ_1 (°) characteristic of the relative arrangement of the rods in the ribbons parallel to [100] are given.

these layers ribbons of molecules (I) parallel to [100] may be distinguished. The relative arrangement of the diacetylene rods in the ribbons satisfies the conditions of topochemical polymerization of symmetrical diacetylenes under control of the crystal lattice (Baughman, 1974). Nevertheless crystal (I) is stable enough and does not undergo polymerization either under visible light irradiation at room temperature or on heating up to ~353 K. The reason for the observed stability possibly lies in the system of rather strong hydrogen bonds, which hinder the cooperative rotation of the molecules around the gravity centres of the diacetylene fragments, thus preventing association into the polydiacetylene chain.

One should note the similarity of the crystal structure of (I) and the non-symmetrically substituted diacetylene (VI) ($\alpha_1 = 4{\cdot}951$ Å, $\gamma_1 = 46{\cdot}1°$) which readily undergoes polymerization in the crystal under UV irradiation or on heating with formation of crystalline polydiacetylene (Matsuda, Nakanishi, Minami & Kato, 1988).



(VI)

In contrast to crystal (I), molecules in crystal (VI) are linked into the 'head-to-head' type dimers. It should also be mentioned that all molecules of (I) belonging to one layer parallel to (010) have the same orientation, whereas in the direction normal to the layer plane (*viz.* along [010]) the orientations of molecules alternate.

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