and stereoisomers, was first isolated in pure form. The hydroxyl H atom in (3) was not located despite the fact that considerable effort was made to do so. However, the closest contact to another molecule for the hydroxyl O(3) atom is 2·58 Å to H(4B), and its closest contact to another O atom is 4·91 Å to O(2)'. Thus there is very little likelihood that this hydroxyl group is involved in any sort of intermolecular interaction. On the other hand, it is well situated for intramolecular hydrogen bonding and given the considerable driving force expected for such an interaction it is plausible that such an interaction is responsible for the anomalous properties and behavior of this compound.

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Structures of Two Isomeric Dihydropyridine Derivatives with S Substituents: Solid-State Allyl Migration

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Abstract. Ethyl 5-cyano-1,4-dihydro-2-methyl-4-phenyl-6-allylthio-3-pyridinecarboxylate, (I), $C_{19}H_{20}N_2O_2S$, $M_r = 340·43$, melting-point range = 358–360 K, monoclinic, $C2/c$, $a = 17·071$ (4), $b = 7·277$ (2), $c = 29·065$ (6) Å, $\beta = 104·96$ (2)°, $V = 3488$ (17) Å³, $Z = 8$, $D_x = 1·296$ g cm⁻³, $\lambda = 0·71069$ Å, $\mu = 1·58$ cm⁻¹, $F(000) = 1440$, $T = 140$ (5) K, $R = 0·059$, $wR = 0·069$ for 299 variables and 2201 unique reflections for which $I > 3\sigma(I)$. On heating continuously at 328 K (I) undergoes a solid-state transformation, forming a product (II) melting in the range 452–453 K whose cell parameters are $a = 17·117$ (8), $b = 7·272$ (4), $c = 29·599$ (11) Å, $\beta = 108·63$ (4)°, $V = 3491$ (42) Å³, $Z = 8$, $D_x = 1·295$ g cm⁻³, $\lambda = 0·71069$ Å. Ethyl 5-cyano-1,4,5,6-tetrahydro-2-methyl-4-phenyl-5-allyl-6-thioxo-3-pyridinecarboxylate, (III), $C_{19}H_{20}N_2O_2S$, $M_r = 340·43$, melting point = 451 K, monoclinic, $P2_1/c$, $a = 11·797$ (1), $b = 12·274$ (2), $c = 13·068$ (3) Å, $\beta = 104·07$ (1)°, $V = 1835$ (6) Å³, $Z = 4$, $D_x = 1·232$ g cm⁻³, $\lambda = 0·71069$ Å, $\mu = 1·49$ cm⁻¹, $F(000) = 720$, $T = 295$ (2) K, $R = 0·036$, $wR = 0·038$ for 325 variables and 1707 unique reflections for which $I > 3\sigma(I)$. The ethyl group of the ethoxycarbonyl substituent in (III) is disordered over two positions. (I) and (III) differ in the position of the allyl group and in the conformation of the ethoxycarbonyl substituent. It is proposed that the (I)→(II) solid-state transformation involves the migration of the propylene chain of the allylthio substituent to the same position it occupies in (III), that the molecular structure of (II) therefore resembles that of (III) and that the molecular packing of (II) resembles that of (I). The molecular structure and the packing of (I), and the relative configuration of the propylene chain in (III), indicate two mechanisms for allyl migration: an intermolecular transfer or an intramolecular Cope rearrangement.

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Introduction. Crystals of ethyl 5-cyano-1,4-dihydro-2-methyl-4-phenyl-6-allythio-3-pyridinecarboxylate (I) were observed to undergo a solid-state transformation to a product (II) (whose crystal structure has yet to be determined), when subjected to continuous heating. While the cell constants of (I) and (II) are very similar, their melting points differ markedly. (I) may also be transformed into the isomeric ethyl 5-cyano-1,4,5,6-tetrahydro-2-methyl-4-phenyl-5-allyl-6-thioxo-3-pyridinecarboxylate (III) by dissolution and subsequent heating in ethanol. In this paper we report the structures of (I) and (III) and attempts to solve the structure of (II) and we propose two possible mechanisms whereby the thermal (I)→(II) transformation might take place.

Experimental. (I): Crystals of (I) were prepared by reaction of ethyl 5-cyano-1,4,5,6-tetrahydro-2-methyl-4-phenyl-6-thioxo-3-pyridinecarboxylate with allyl bromide in basic medium as shown in the reaction scheme [Goncharenko, Promonenkov, Sharanin, Shestopalov & Litvinov, 1988, 1990 (private communication)].

(I)

(III)
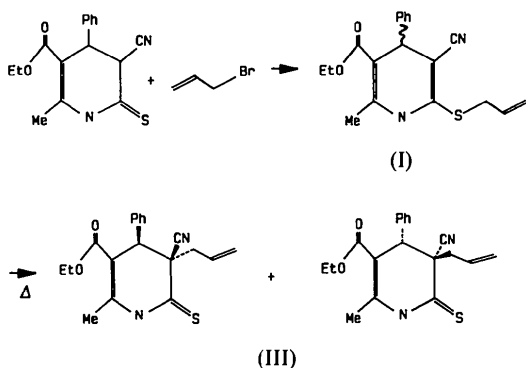
An elongated platelet-like bright yellow crystal, $0.20 \times 0.3 \times 0.4$ mm, was mounted on the end of a quartz fibre. Enraf–Nonius CAD-4 diffractometer. Unit-cell data from 25 reflections with $4 < \theta < 23°$. Data were collected in two parts at $T = 140$ K. For the first part (a): $2 \le \theta \le 25°$, ω scan, $(2.40 + 0.34\tan\theta)°$, with $-20 \le h \le 20$, $0 \le k \le 8$, $0 \le l \le 34$, 2719 unique reflections ($R_{int} = 0.016$). Before completing data collection in this range the crystal broke. Measurements were continued on the remaining fragment, (b): $20 \le \theta \le 27°$, ω scan, $(2.40 + 0.34\tan\theta)°$, with $-20 \le h \le 20$, $0 \le k \le 8$, $0 \le l \le 34$, 1415 unique reflections ($R_{int} = 0.091$). In both cases three intensity control reflections (311, 15,3,3, 608) were measured. For part (a) $F_{obs} = 165$ (1), 117 (2) and 153 (2), respectively, while for part (b) $F_{obs} = 101$ (1), 69 (1), 93 (8). After scaling part (b) by a factor of 1.65 a merged data set with 4134 entries was obtained, of which 2201 unique reflections had $I > 3\sigma(I)$. The data were corrected for extinction but not for absorption and the structure was solved by direct methods as implemented in *SHELXS*86 (Sheldrick, 1986). H atoms were all located from difference maps and refined isotropically; non-H atoms were treated anisotropically. The refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = 4.8/[\sigma^2(F) + 0.0006F^2]$, *SHELX*76 system of programs (Sheldrick, 1976). Final $R = 0.059$, $wR = 0.069$ for 299 parameters. Largest Δ/σ for the final cycle of refinement was 0.02 and the final $\Delta\rho_{max} = 0.59$ e Å^{-3} is located 0.96 Å from the S atom. The molecule exhibits no unexpected or unusual bond distances, angles or displacement parameters.

(II): Crystals of (I) were kept in a drying oven at 328 K, *i.e.* at a temperature which is ~30 K lower than the melting temperature of (I). After 12 h their melting-point range had stabilized at 452–453 K, and the previously bright crystals had dulled somewhat, while maintaining their integrity and colour. A crystal, $0.3 \times 0.3 \times 0.5$ mm, was mounted on the end of a quartz fibre. Enraf–Nonius CAD-4 diffractometer. Unit-cell data from 25 reflections with $3 < \theta < 21°$, $T = 140$ K. Data collection in ω-scan mode was attempted. The backgrounds were high and very asymmetric. From a total of 5748 reflections, 2115 showed $I \ge 3\sigma(I)$. But the data set was of dubious quality. Several attempts to solve the structure using Patterson search methods (*PATSEE*; Egert & Sheldrick 1985) with various molecular fragments of (III) failed. Additional experimental work is now being performed in the Moscow laboratories.

(III): Dissolution of (I) in ethanol at 351 K followed by evaporation yielded a yellow powder. On recrystallization from a 1:1 mixture of chloroform and benzene well-shaped crystals of (III) were obtained. An elongated platelet-like bright yellow crystal ($0.1 \times 0.4 \times 0.28$ mm) was mounted on the end of a quartz fibre. Enraf–Nonius CAD-4 diffractometer. Unit-cell data from 14 reflections with $13 < \theta < 16°$. Data collection was performed at room temperature, after numerous attempts at obtaining low-temperature data had failed due to the instability of crystal orientation. Data collection for $1 \le \theta \le 25°$ by ω scan, $(1.40 + 0.35\tan\theta)°$, with $0 \le h$, $k \le 14$, $-15 \le l \le 15$. Four intensity control reflections (0,12,0, 812, 106 and 102) remained constant throughout. 3057 reflections measured, with 2571 unique ($R_{int} = 0.027$), of which 1707 have $I > 3\sigma(I)$. The data were corrected for extinction but not for absorption and the structure was solved using direct methods as implemented in *SHELXS*86 (Sheldrick, 1986). H atoms were initially all located from difference maps, except for those on the ethoxy-carbonyl substituent. The terminal methyl C atom of this group is disordered over two positions by rotation about the O—CH$_2$ bond; the site occupancy factors (s.o.f.) for these two positions were refined to

0·60 (2) and 0·40, for positions A and B, respectively. Once the s.o.f.'s had been refined, H atoms restrained to idealized CH_3 and CH_2 geometries were added for the terminal methyl and the methylene groups in both disordered positions. For the sake of consistency all H's attached to terminal C atoms were similarly restrained to idealized geometries and refined isotropically with all H's within a given group having the same displacement parameter [the C—H distance refined to 0·973 (12) Å]. All non-H atoms were refiend anisotropically. The refinement minimized $\Sigma w(|F_o| - |F_c|)^2$, $w = 1\cdot8/[\sigma^2(F) + 0\cdot0001F^2]$, SHELX76 system (Sheldrick, 1976). Final $R = 0\cdot036$, $wR = 0\cdot038$ for 325 parameters. Largest Δ/σ for final cycle of refinement was 0·09 and the final $\Delta\rho_{max} = 0\cdot13$ e Å^{-3} located in the region of the disorder. The structure exhibits no unusual or unexpected bond distances or angles. The displacement parameters for the methyl group and the methylene protons in position B (s.o.f. = 0·40) are larger than those for the same atoms in the more populated position A (s.o.f. = 0·60) with some correlation among the coordinates, displacement parameters and the s.o.f. ($\sim 0\cdot75$).

Final positional coordinates and equivalent isotropic displacement parameters for the non-H atoms of (I) and (III) are given in Table 1.* Fig. 1 depicts stereoviews of the molecular structures of (I) and (III) (only position A of the ethoxycarbonyl substituent is represented) and shows the numbering schemes used.

Discussion. The major difference between the two isomers lies in the position of the propylene fragment. In (I) the propylene chain is bound to the S atom at C1, while in (III) it has migrated to C2. Accompanying this shift the C1—C2 bond has changed from a double [1·351 (6) Å] to a single [1·529 (4) Å] bond, the C1—S bond from a single [1·753 (4) Å] to a double [1·626 (3) Å] bond. The different position of the propylene fragment in (I) and (III) is clearly a consequence of the dissolution and subsequent heating of (I).

Thus far we have not been able to solve the structure of (II). Solution IR and NMR spectra reveal, however, that the molecular connectivities of (II) and (III) are identical (Litvinov, Sharanin, Shestopalov & Goncharenko, 1990). This suggests that the thermally induced (I)→(II) solid-state transformation involves the same allyl migration as does the (I)→(III) transformation. On the other hand the

Table 1. *Final atomic positional coordinates and B_{eq} values with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Compound (I)				
S	0·2319 (1)	0·2276 (2)	0·56680	2·63 (2)
O1	0·0725 (2)	0·9910 (4)	0·6326 (1)	2·29 (6)
O2	−0·0053 (2)	0·7829 (4)	0·6564 (1)	2·47 (6)
N1	0·1249 (2)	0·3630 (5)	0·6117 (1)	1·73 (6)
N2	0·3259 (2)	0·6890 (6)	0·5545 (1)	3·43 (8)
C1	0·1887 (2)	0·4054 (6)	0·5927 (1)	1·75 (7)
C2	0·2163 (2)	0·5800 (6)	0·5947 (1)	1·84 (8)
C3	0·1880 (2)	0·7235 (6)	0·6252 (1)	1·56 (6)
C4	0·1027 (2)	0·6756 (5)	0·6274 (1)	1·46 (6)
C5	0·0753 (2)	0·5003 (6)	0·6223 (1)	1·57 (7)
C6	−0·0063 (3)	0·4292 (7)	0·6244 (2)	2·05 (8)
C7	0·2766 (2)	0·6347 (6)	0·5714 (1)	2·37 (8)
C8	0·1420 (3)	0·1097 (6)	0·5305 (1)	2·53 (8)
C9	0·0860 (3)	0·2334 (6)	0·4971 (1)	2·79 (9)
C10	0·0095 (3)	0·2581 (7)	0·4977 (2)	3·25 (9)
C11	0·0556 (2)	0·8310 (6)	0·6380 (1)	1·69 (7)
C12	−0·0538 (3)	0·9289 (6)	0·6694 (2)	2·57 (9)
C13	−0·1117 (3)	0·8357 (7)	0·6925 (2)	2·9 (1)
C14	0·2481 (2)	0·7386 (5)	0·6743 (1)	1·57 (6)
C15	0·3218 (2)	0·8273 (6)	0·6784 (1)	1·92 (7)
C16	0·3794 (2)	0·8335 (6)	0·7217 (1)	1·97 (8)
C17	0·3634 (2)	0·7536 (6)	0·7617 (1)	2·13 (7)
C18	0·2898 (2)	0·6695 (6)	0·7581 (1)	1·95 (7)
C19	0·2323 (2)	0·6623 (6)	0·7149 (1)	1·83 (7)
Compound (III)				
S	0·0164 (1)	0·3221 (1)	0·0964 (1)	5·58 (2)
O1	0·3379 (2)	−0·1143 (2)	0·3047 (2)	5·77 (5)
O2	0·2994 (2)	−0·0289 (2)	0·4417 (2)	5·58 (5)
N1	0·1159 (2)	0·1292 (2)	0·1197 (2)	3·54 (5)
N2	0·0512 (2)	0·1242 (2)	−0·1225 (2)	3·91 (5)
C1	0·0711 (2)	0·2142 (2)	0·1624 (2)	3·27 (5)
C2	0·0718 (2)	0·1954 (2)	0·2782 (2)	2·79 (5)
C3	0·1873 (2)	0·1411 (2)	0·3402 (2)	2·84 (5)
C4	0·2171 (2)	0·0452 (2)	0·2786 (2)	3·04 (5)
C5	0·1827 (2)	0·0429 (2)	0·1734 (2)	3·14 (5)
C6	0·2095 (3)	−0·0410 (2)	0·0990 (2)	4·45 (7)
C7	0·0584 (2)	0·2999 (2)	0·3294 (2)	3·01 (5)
C8	−0·0337 (3)	0·1210 (2)	0·2840 (2)	3·39 (6)
C9	−0·1505 (3)	0·1637 (3)	0·2300 (3)	4·49 (7)
C10	−0·2322 (3)	0·1073 (4)	0·1690 (3)	6·5 (1)
C11	0·2902 (3)	−0·0418 (2)	0·3392 (2)	3·69 (6)
C12	0·3679 (4)	−0·1093 (3)	0·5122 (3)	7·4 (1)
C13A*	0·396 (1)	−0·0631 (9)	0·6161 (6)	6·6 (2)
C13B*	0·335 (3)	−0·105 (3)	0·607 (2)	17·4 (9)
C14	0·2886 (2)	0·2196 (2)	0·3731 (2)	3·20 (5)
C15	0·3261 (3)	0·2513 (3)	0·4773 (2)	4·13 (7)
C16	0·4177 (3)	0·3228 (3)	0·5095 (3)	5·59 (8)
C17	0·4724 (3)	0·3638 (3)	0·4378 (4)	5·7 (1)
C18	0·4380 (3)	0·3341 (3)	0·3338 (3)	5·49 (9)
C19	0·3465 (3)	0·2615 (3)	0·3022 (3)	4·55 (7)

* Atoms denoted by A have s.o.f. = 0·6, those by B have s.o.f. = 0·4 (see text).

very close similarity in the cell constants of (I) and (II) suggests that their molecular packing is similar and that a comparison of the packing in (I) and (II) might eventually provide evidence for the mechanism involved in the migration of the propylene chain.

An examination of the molecular structure and packing of (I) already suggests two possibilities. Fig. 2 illustrates a stereoview of two of the eight molecules in the unit cell, related to each other by the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$. Quite clearly the terminal C atom (C10) of the propylene chain is in a position to attach itself to C2 via either an intramolecular Cope rearrangement (dashed line, C10···C2 distance = 4·556 Å) or an intermolecular transfer (dotted line, C10···C2' distance = 4·256 Å).

There are no other C2 atoms within 6·0 Å of C10. That the phase transformation may well occur *via* either of these two paths in the solid state is substantiated by the *trans* configuration (with respect to the phenyl substituent) of the propylene chain in (III). Fig. 2 shows that the propylene chain ought to be in this configuration irrespective of the path taken in the transformation. One might argue that H102 on C10 is pointing almost exactly at C2' (the distance H102···C2' is 3·37 Å) and that therefore an intermolecular mechanism is unlikely. However, this would seem to be a weak argument, since the conformational changes and reorientations of the entire molecule necessary for the transformation may well improve this unfavourable situation in the starting material. A clear distinction between the two mechanisms could, for instance, be obtained *via* isotropic double labelling experiments in which both the propylene chain and the remainder of the molecule carry appropriate labels.

Solid-state Cope rearrangements have previously been observed in at least four cases: in the transformation of (photochemically produced) *cis*-1,2-divinylcyclobutanes into cyclooctadienes (Green, Lahav & Schmidt, 1971); in semibullvalene (Macho, Miller & Yannoni, 1983); in substituted semibullvalene (Jackman, Benesi, Mayer, Quast, Peters, Peters & von Schnering, 1989); and in bullvalene (Meier & Earl, 1985).

A second significant difference between (I) and (III) lies in the relative orientation of the ethoxycarbonyl substituent. In (I) the torsion angle C3—C4—C11—O1 = 19·6°, whereas in (III) it is −167·3°. The latter conformation is also found in the closely related ethyl 3-cyano-6-methyl-2-oxo-4-(3-pyridyl)-3,4-dihydro-5-pyridinecarboxylate (Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1978) in which the corresponding torsion angle in the corresponding enantiomer has a value of −174·1°. Perhaps the two different crystalline modifications of (II) and (III), as evidenced by very different cell parameters, are connected to the adoption of different conformations by the ethoxycarbonyl substituent.
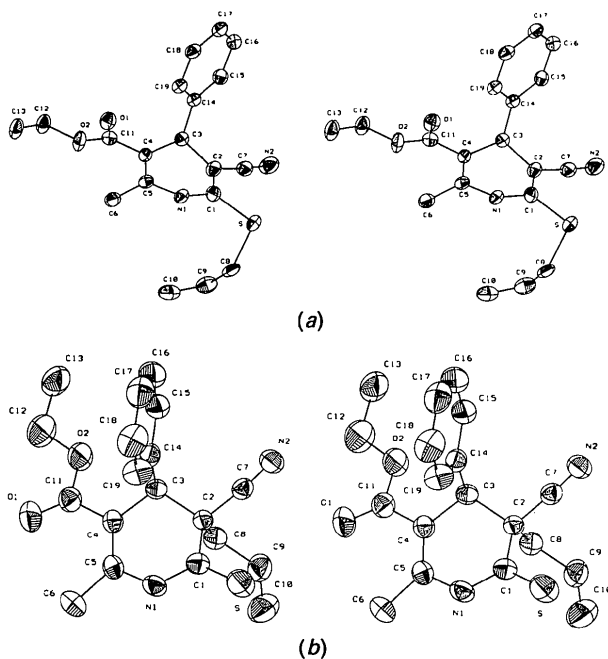

Fig. 1. Stereoview of (I) (*a*) and (III) (*b*) with atomic numbering, 50% probability ellipsoids.
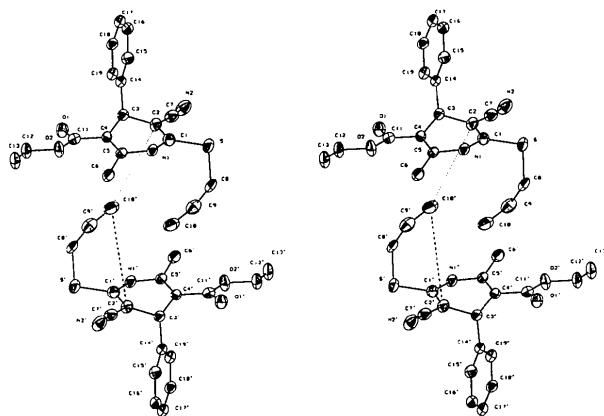

Fig. 2. Stereoview of two molecules of (I), related *via* a centre of symmetry.

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