

good biological activity by the formation of an intramolecular O—H...N(1) bond analogous to the intramolecular hydrogen bonds in ureido purines (Parthasarathy *et al.*, 1974).

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References

- BELT, J. A. (1984). *Mol. Pharmacol.* In the press.
 BROWN, G. M. (1969). *Acta Cryst.* B25, 1338–1353.
 CASS, C. E., GAUDETTE, L. A. & PATERSON, A. R. P. (1974). *Biochim. Biophys. Acta*, 345, 1–10.
 COCHRAN, W. (1948). *Acta Cryst.* 1, 138–142.
 DEXTER, D. D. (1972). *Acta Cryst.* B28, 49–54.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
 GINELL, S. L. & PARTHASARATHY, R. (1978). *Biochem. Biophys. Res. Commun.* 84, 886–894.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98 and 148–151. Birmingham: Kynoch Press.
 JARVIS, S. M., JANMOHAMED, S. N. & YOUNG, J. D. (1983). *Biochem. J.* In the press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KOREN, R. M., PATERSON, A. R. P. & CASS, C. E. (1983). *Biochem. J.* In the press.
 MUNNS, A. R. I. & TOLLIN, P. (1970). *Acta Cryst.* B26, 1101–1113.
 NAGASHIMA, N. & IITAKA, Y. (1968). *Acta Cryst.* B24, 1136–1138.
 NAGASHIMA, N. & WAKABAYASHI, K. (1974). *Acta Cryst.* B30, 1094–1099.
 NAGASHIMA, N., WAKABAYASHI, K., MATSUZAKI, T. & IITAKA, Y. (1974). *Acta Cryst.* B30, 320–326.
 PARTHASARATHY, R., OHRT, J. M. & CHHEDA, G. B. (1974). *J. Am. Chem. Soc.* 96, 8087–8094.
 PATERSON, A. R. P., JAKOBS, E. S., HARLEY, E. R., CASS, C. E. & ROBINS, M. J. (1983). *Development of Target-Oriented Anticancer Drugs*, edited by Y.-C. CHENG, B. GOZ & M. MINKOFF, pp. 41–56. New York: Raven Press.
 PATERSON, A. R. P., JAKOBS, E. S., HARLEY, E. R., FU, N.-W., ROBINS, M. J. & CASS, C. E. (1983). *Regulatory Function of Adenosine*, edited by R. M. BERNE, T. W. RALL & R. RUBIO, pp. 203–229. The Hague: Martinus Nijhoff.
 PATERSON, A. R. P., KOLASSA, N. & CASS, C. E. (1981). *Pharmacol. Ther.* 12, 515–536.
 PATERSON, A. R. P., NAIK, S. R. & CASS, C. E. (1977). *Mol. Pharmacol.* 13, 1014–1023.
 PAUL, B., CHEN, M. F. & PATERSON, A. R. P. (1975). *J. Med. Chem.* 18, 968–973.
 PLAGEMANN, P. G. W. & WOHLHEUTER, R. M. (1980). *Curr. Top. Membr. Transp.* 14, 225–330.
 RAO, S. T. & SUNDARALINGAM, M. (1970). *J. Am. Chem. Soc.* 92, 4963–4970.
 SHEFTER, E. (1968). *J. Pharm. Sci.* 57, 1157–1162.
 SKOOG, F., HAMZI, H. Q., SZWEYKOWSKA, A. M., LEONARD, N. J., CARRAWAY, K. L., FUJI, T., HEGELSON, J. P. & LOEPPKY, R. N. (1967). *Phytochemistry*, 6, 1169–1192.
 SLETTEN, E., SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* B25, 1330–1338.
 SORIANO-GARCIA, M. & PARTHASARATHY, R. (1975). *Biochem. Biophys. Res. Commun.* 64, 1062–1068.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
 SUBRAMANIAN, E., MADDEN, J. J. & BUGG, C. E. (1973). *Biochem. Biophys. Res. Commun.* 50, 691–696.
 THEWALT, U., BUGG, C. E. & MARSH, R. E. (1970). *Acta Cryst.* B26, 1089–1101.

Acta Cryst. (1984). C40, 1901–1905

A Thermal Molecular Migration in the Solid State. Structures of Isomeric 5-Amino-4-(2,6-dichlorophenyl)-1-(2-nitrophenyl)-1*H*-1,2,3-triazole (Yellow Form I) and 4-(2,6-Dichlorophenyl)-5-(2-nitroanilino)-2*H*-1,2,3-triazole (Red Form II), C₁₄H₉Cl₂N₅O₂

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Abstract. Yellow form (I): $M_r = 350.09$, monoclinic, $P2_1/n$, $Z = 4$, $a = 9.525$ (1), $b = 14.762$ (1), $c = 11.268$ (1) Å, $\beta = 107.82$ (1)°, $V = 1508.3$ Å³, D_m (flotation in aqueous KI) = 1.539 (2), $D_x = 1.541$ (2) g cm⁻³, $\mu(\text{Cu K}\alpha, \lambda = 1.5418 \text{ \AA}) = 40.58 \text{ cm}^{-1}$, $F(000) = 712$, $T = 293 \text{ K}$, $R = 8.8\%$ for 2054 significant reflections. Red form (II): $M_r = 350.09$, triclinic, $P\bar{1}$, $Z = 2$, $a = 9.796$ (2), $b = 10.750$ (2), $c = 7.421$ (1) Å, $\alpha = 95.29$ (2), $\beta =$

70.18 (1), $\gamma = 92.76$ (2)°, $V = 731.9$ Å³, D_m (flotation in KI) = 1.585 (3), $D_x = 1.588$ (3) g cm⁻³, $\mu(\text{Cu K}\alpha, \lambda = 1.5418 \text{ \AA}) = 40.58 \text{ cm}^{-1}$, $F(000) = 356$, $T = 293 \text{ K}$, $R = 5.8\%$ for 1866 significant reflections. There are no unusual bond distances or angles. The triazole and two phenyl rings are planar. On the basis of packing considerations the possibility of intermolecular interactions playing a role in the reactivity of the starting material is ruled out.

Introduction. The thermal molecular migration of substituted 5-amino-1,2,3-triazoles involves the Dimroth or amidine rearrangement (Dimroth, 1909) which has been extensively studied both in solution and in homogeneous melt (Brown, 1968).

Crystals of yellow form (I) were observed to undergo an irreversible isomerization on heating to the red form (II). This conversion also takes place on heating (I) with acetic acid during recrystallization or with a mixture of methanol and acetic acid (Joshi, 1981).

A single crystal of form (I) (0.3–0.5 mm in length) was heated in a differential scanning calorimeter (DSC-2 Perkin Elmer) and observed under a polarizing microscope. From room temperature (273 K) to 398 K the crystal showed no indication of melting, softening or colour change and showed the same extinction direction between crossed polaroids. However, at 401 K a minor imperfection (which had shown no extinction) showed signs of having turned into an orange-coloured opaque region. The rest of the crystal remained intact. On continued heating to 403 K, the opaque nature seemed to spread at random points in the crystal with no identifiable face, edge or corner as the front for nucleation. The original faces and morphology of the crystal were retained. Heating then in intervals of 2 K to 413 K showed increasing numbers of opaque orange-coloured regions spreading in a random manner. At 423 K, when a fair amount of the original yellow crystal had been converted to orange, an X-ray photograph on a Weissenberg camera showed that the original single crystal had become polycrystalline. Subsequent heating to 463 K deepened the colour to reddish intensity as was seen in the solution conversion to red form (II) from yellow form (I) in methanol/acetic acid medium.

Powder diffraction patterns of well powdered samples of red form (II) as obtained from solution and of that obtained by rearrangement in the solid state (463 K) showed distinct similarities. The powder diffraction pattern of the sample at 423 K showed lines corresponding also to the original yellow form (I).

X-ray crystallographic investigations were undertaken with the aim of understanding this potential solid-state reaction in terms of the molecular geometry of the reactant. Also, it was necessary to discover whether the solid-state reaction is in any way related to the molecular packing of the reactant molecules although the Dimroth rearrangement based on solution-phase chemistry is known to involve intramolecular migration of groups.

Experimental. Yellow single crystals of (I) were obtained from acetone by slow evaporation and those of (II) (obtained by solution rearrangement in methanol/acetic acid) were recrystallized from methanol. Crystals approx. 0.1 × 0.5 × 0.7 mm (I) and 0.1 × 0.2 × 0.4 mm (II). Preliminary Weissenberg photographs indicated that the crystals are monoclinic

(I) and triclinic (II). Nonius CAD-4 diffractometer. Lattice parameters refined using a least-squares fit to the settings for 16 (I) and 25 (II) accurately centred reflections. Graphite-monochromated Cu K α radiation. $\omega/2\theta$ scan mode, $\theta \leq 60^\circ$ [for (I) and (II)]. Two standard reflections [12 $\bar{2}$, 223 for (I) and 331, 122 for (II)] showed only statistical variation within $\pm 2\%$. Total of 2574 (I) and 2390 (II) reflections collected of which 2054 (I) and 1866 (II) considered significant [$|F_o| \geq 3\sigma(|F_o|)$]. Data not corrected for absorption. Both structures solved by direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0.088$, $R_w = 0.092$, $S = 1.83$ for (I) and $R = 0.058$, $R_w = 0.062$, $S = 1.54$ for (II); $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1.0000/[\sigma^2(F) + 0.0002|F_o|^2]$ for (I) and $w = 1.4593/[\sigma^2(F) + 0.00187|F_o|^2]$ for (II). *SHELX*76 (Sheldrick, 1976) was used for full-matrix refinement. Δ/σ for non-hydrogen atoms for (I) was about 0.004 and for (II) about 0.003. Final difference maps of (I) and (II) featureless. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Figures were drawn with *ORTEP*II (Johnson, 1976).

Discussion. Perspective views and the numbering schemes with bond lengths and angles for non-hydrogen atoms for compounds (I) and (II) are shown in Figs. 1 and 2 respectively. Positional coordinates of non-hydrogen atoms for (I) and (II) are in Tables 1 and 2 respectively.*

The bond lengths and angles of the triazole moiety in yellow form (I) closely approximate those of ethyl 5-amino-1*H*-1,2,3-triazole-4-carboxylate (Párkányi, Kálmán, Argay & Schwartz, 1977) in which the double bond between N(2) and N(3) [1.310 (5) Å] is as short as in the yellow form (I) [1.305 (5) Å]. In 5-mesylamino-2*H*-1,2,3-triazole-4-carbonitrile monohydrate (Kálmán, Párkányi, Schwartz & Simon, 1976) the N(2)–N(3) bond length is also found to be 1.310 (5) Å.

The geometry of the triazole moiety in red form (II) is compared with the crystal structures of compounds containing the 2*H*-1,2,3-triazole moiety reported in the literature (Kozłowski, Singh & Hodgson, 1974; Foces-Foces, Cano & García-Blanco, 1975*a,b*; Singh &

* Lists of structure factors, anisotropic thermal parameters, intermolecular separations, H-atom positions and their isotropic temperature factors, and bond lengths and angles for H atoms for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39615 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Hodgson, 1975; López de Lerma, Cano, García-Blanco & Martínez-Ripoll, 1976; Kálmán, Párkányi, Schawartz & Simon, 1976; Kálmán, Párkányi & Schawartz, 1977; Harlow, Brown, Dewar & Simonsen, 1977; Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977; Wang, Harlow & Simonsen, 1979). Although the substituents vary widely and seven of the

compounds involve a six-membered ring fused to a five-membered ring, the mean geometries of the triazole ring are quite similar; the overall weighted average distances and angles for ten structures are: N–N 1.332 (4), C–N 1.338 (5), C–C 1.394 (5) Å; N–N 116.6 (3), C–N–N 102.7 (4), C–C–N 109.0 (3)°.

In both forms the triazole and the two phenyl rings are planar, within experimental limits of error. In form (I), the phenyl rings, one attached to N(1) and the other attached to C(1), are inclined to the triazole ring at angles of 81.7 and 86.1° respectively. However, in form (II) the phenyl ring attached to C(2) is tilted at 71.7° to the triazole ring whereas the other phenyl ring is at 23.8°. In (I), the nitro group makes an angle of 24.5° with the phenyl ring whereas this angle is 1.1° in form (II).

The Dimroth rearrangement which refers to an isomerization preceded by ring fission and subsequent recyclization is understood in terms of electronic effects (Dimroth, 1909). The polarization of the N(1)–N(2) bond, which is necessary for ring fission, would be encouraged in yellow form (I) by strong π -electron localization in the double-bonded nitrogen atoms N(2) and N(3). The N(1)–N(2) bond in form (I) [1.366 (4) Å] is slightly longer than the value reported for the N–N bond in pyrazole [1.352 (6) Å, La Cour & Rasmussen (1973)].

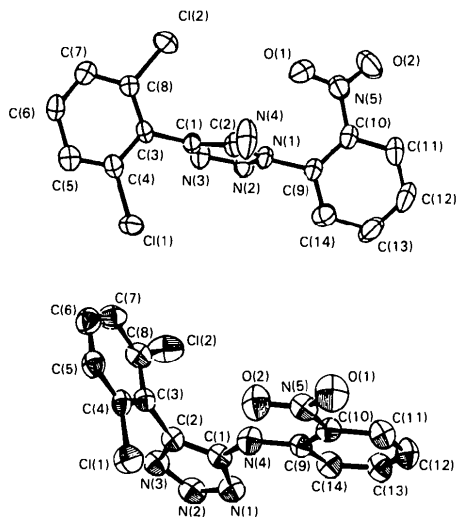


Fig. 1. Perspective views of molecules (I) (top) and (II) (bottom).

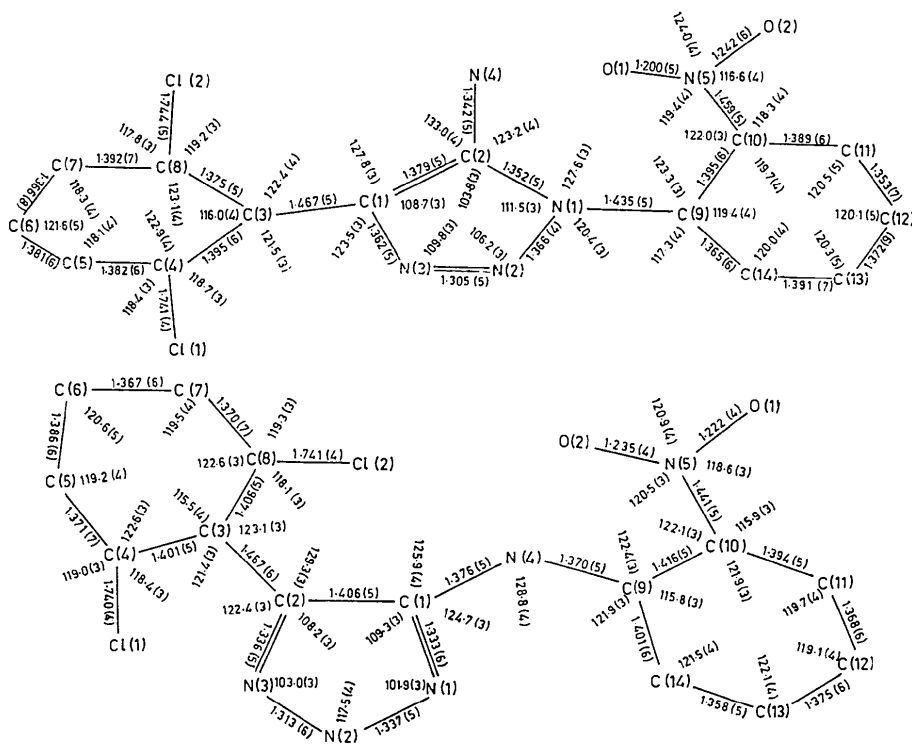


Fig. 2. Bond lengths and angles of non-hydrogen atoms with the numbering scheme for yellow form (I) (top) and red form (II) (bottom). (Values in Å and deg, with e.s.d.'s in parentheses.)

Table 1. Final (fractional) coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms in yellow form (I)

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

	x	y	z	U _{eq} (Å ²)
C(4)	9055 (4)	1713 (3)	2020 (3)	4.01 (0.13)
C(3)	8559 (4)	1430 (2)	3003 (3)	3.33 (0.12)
C(8)	8593 (4)	512 (3)	3217 (3)	4.05 (0.13)
C(7)	9090 (5)	-112 (3)	2510 (4)	5.48 (0.18)
C(6)	9577 (5)	206 (3)	1566 (4)	5.27 (0.17)
C(5)	9544 (4)	1117 (3)	1285 (3)	4.52 (0.14)
Cl(1)	9061 (1)	2867 (1)	1700 (1)	5.29 (0.05)
Cl(2)	7989 (1)	96 (1)	4425 (1)	6.17 (0.05)
C(1)	8080 (4)	2082 (2)	3783 (3)	3.30 (0.12)
N(3)	6676 (3)	2404 (2)	3500 (3)	4.33 (0.12)
N(2)	6577 (4)	2973 (2)	4358 (3)	4.41 (0.12)
N(1)	7949 (3)	3011 (2)	5213 (3)	3.47 (0.10)
C(2)	8914 (4)	2468 (3)	4888 (3)	3.80 (0.13)
N(4)	10351 (4)	2421 (3)	5539 (4)	6.82 (0.18)
C(9)	8263 (4)	3656 (2)	6213 (3)	3.75 (0.13)
C(14)	8489 (5)	4533 (3)	5935 (4)	5.18 (0.16)
C(13)	8732 (6)	5198 (3)	6851 (5)	6.39 (0.20)
C(12)	8771 (6)	4973 (3)	8042 (5)	6.32 (0.20)
C(11)	8558 (5)	4105 (3)	8329 (5)	5.40 (0.18)
C(10)	8286 (4)	3435 (3)	7422 (4)	4.00 (0.13)
N(5)	8032 (4)	2512 (3)	7773 (3)	4.80 (0.13)
O(1)	8276 (4)	1887 (2)	7184 (3)	6.44 (0.14)
O(2)	7546 (5)	2429 (3)	8673 (3)	7.89 (0.17)

Table 2. Final (fractional) coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms in red form (II)

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

	x	y	z	U _{eq} (Å ²)
C(8)	2677 (4)	489 (3)	9790 (5)	4.01 (0.13)
C(3)	1627 (3)	1410 (3)	10635 (5)	3.78 (0.13)
C(4)	1064 (4)	1498 (4)	12647 (6)	4.50 (0.14)
C(5)	1510 (4)	747 (5)	13730 (6)	5.47 (0.17)
C(6)	2528 (5)	-160 (4)	12810 (7)	5.42 (0.17)
C(7)	3119 (4)	-281 (4)	10850 (6)	4.86 (0.16)
Cl(2)	3455 (1)	351 (1)	7297 (1)	6.20 (0.04)
Cl(1)	-222 (1)	2630 (1)	13809 (1)	6.96 (0.05)
C(2)	1136 (3)	2231 (3)	9513 (5)	3.73 (0.12)
C(1)	1861 (3)	3250 (3)	8510 (5)	3.73 (0.12)
N(1)	983 (3)	3777 (3)	7778 (5)	4.77 (0.13)
N(2)	-217 (4)	3063 (4)	8368 (5)	5.12 (0.14)
N(3)	-193 (3)	2132 (3)	9383 (5)	4.71 (0.12)
N(4)	3267 (3)	3637 (3)	8269 (5)	4.46 (0.13)
C(9)	3918 (3)	4771 (3)	7775 (5)	3.54 (0.12)
C(14)	3136 (4)	5778 (4)	7581 (6)	4.37 (0.14)
C(13)	3782 (4)	6908 (4)	7137 (6)	5.10 (0.16)
C(12)	5241 (5)	7116 (4)	6793 (6)	5.29 (0.17)
C(11)	6062 (4)	6166 (4)	6957 (6)	4.67 (0.15)
C(10)	5413 (3)	5007 (3)	7450 (5)	3.53 (0.12)
N(5)	6356 (3)	4064 (3)	7607 (4)	4.30 (0.12)
O(1)	7631 (3)	4338 (3)	7334 (5)	6.60 (0.14)
O(2)	5880 (3)	3003 (3)	8011 (5)	6.37 (0.13)

Table 3. Some important torsion angles (°) with e.s.d.'s in parentheses

Yellow form (I)	
C(4)–C(3)–C(1)–N(3)	87.4 (4)
C(2)–N(1)–C(9)–C(14)	94.2 (5)
C(9)–C(10)–N(5)–O(1)	24.5 (6)
Red form (II)	
C(8)–C(3)–C(2)–C(1)	-73.7 (5)
N(1)–C(1)–N(4)–C(9)	20.5 (6)
C(1)–N(4)–C(9)–C(14)	5.2 (6)
C(11)–C(10)–N(5)–O(1)	1.1 (5)

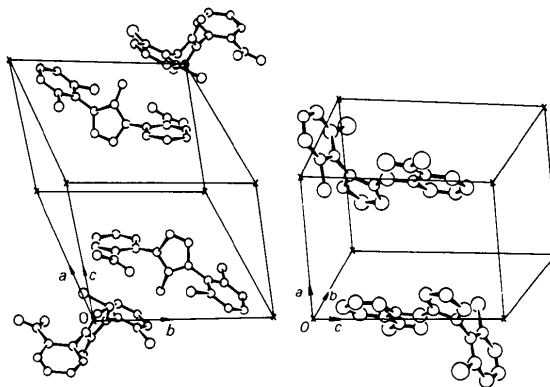


Fig. 3. Packing of the yellow form (I) (left) viewed down a and of the red form (II) (right) viewed down b.

The possibility of intermolecular interactions playing a critical role in the observed reactivity in the solid state was investigated. We do not find any intermolecular short contacts of special significance involving atoms of the triazole ring. Thus it is reasonable to conclude that intermolecular interactions do not play any significant role in the reactivity of the yellow form (I).

It is perhaps of significance for the reaction pathway that there is a short intramolecular contact between N(1) and O(1) [2.713 (4) Å], the angle N(5)–O(1)···N(1) being 89.1 (4)°. The lone pair of O(1) is in the direction of N(1). The packing of both forms is shown in Fig. 3.

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References

- BROWN, D. J. (1968). *Mechanisms of Molecular Migrations*, Vol. 1, edited by B. S. THYAGARAJAN, pp. 209–245. New York: Interscience.
- DIMROTH, O. (1909). *Justus Liebigs Ann. Chem.* **364**, 183.
- FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1975a). *Acta Cryst.* **B31**, 1427–1429.
- FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1975b). *Acta Cryst.* **B31**, 2245–2249.
- HARLOW, R. L., BROWN, S. B., DEWAR, H. J. S. & SIMONSEN, S. H. (1977). *Acta Cryst.* **B33**, 3423–3428.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- JOSHI, B. S. (1981). Unpublished results.
- KÁLMÁN, A., PÁRKÁNYI, L. & SCHAWARTZ, J. (1977). *Acta Cryst.* **B33**, 3097–3102.
- KÁLMÁN, A., PÁRKÁNYI, L., SCHAWARTZ, J. & SIMON, K. (1976). *Acta Cryst.* **B32**, 2245–2247.
- KOZŁOWSKI, D. L., SINGH, P. & HODGSON, D. J. (1974). *Acta Cryst.* **B30**, 2806–2811.
- LA COUR, T. & RASMUSSEN, S. E. (1973). *Acta Chem. Scand.* **27**, 1845–1854.
- LÓPEZ DE LERMA, J., CANO, F. H., GARCÍA-BLANCO, S. & MARTÍNEZ-RIPOLL, H. (1976). *Acta Cryst.* **B32**, 3019–3022.

- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1977). *Acta Cryst.* B33, 500–504.
- PÁRKÁNYI, L., KÁLMÁN, A., ARGAY, GY. & SCHAWARTZ, J. (1977). *Acta Cryst.* B33, 3102–3106.
- SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination, Univ. of Cambridge, England.
- SINGH, P. & HODGSON, D. J. (1975). *Acta Cryst.* B31, 845–851.
- WANG, T. H., HARLOW, R. L. & SIMONSEN, S. H. (1979). *Acta Cryst.* B35, 223–225.

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Conformational Flexibility in Androgenic Steroids: The Structure of a New Form of (+)-17 β -Hydroxy-19-nor-4-androsten-3-one (19-Nortestosterone), C₁₈H₂₆O₂

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Abstract. The structure and conformation of a second crystalline modification of 19-nortestosterone has been determined by X-ray methods. $M_r = 274$, monoclinic $P2_1$, $a = 9.755$ (2), $b = 11.467$ (3), $c = 14.196$ (3) Å, $\beta = 101.07$ (2)°, $V = 1558.4$ (8) Å³, $Z = 4$, $D_x = 1.168$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.80$ cm⁻¹, $F(000) = 600$, $T = 300$ K. $R = 0.060$ for 2158 observed reflections. The two molecules in the asymmetric unit show significant differences in the A-ring conformation from that of the previously reported form of the title compound [Precigoux, Busetta, Courseille & Hospital (1975). *Acta Cryst.* B31, 1527–1532]. The 1 α ,2 β -half-chair conformation of the A ring increases its conformational freedom compared with testosterone.

Introduction. Testosterone (I), a testicular sex hormone, is a strong androgenic and anabolic agent, whereas 19-nortestosterone (II), identical to testosterone except for the absence of the angular methyl group on C(10), retains anabolic activity of the same order as (I) but androgenic activity is reduced considerably (Herschberger, Shipley & Meyer, 1953; Barnes, Stafford, Guild, Thole & Olson, 1954). It is of interest to determine the conformational features of 19-nortestosterone accurately and compare them with those of testosterone. Several crystallographic investigations of testosterone are known (Duax & Norton, 1975) but so far only one crystal structure of 19-nortestosterone has been studied (Precigoux *et al.*, 1975), where atoms of ring A are disordered. Since it is known from the literature that steroids often exhibit polymorphism depending on the solvent of crystallization (Busetta, Courseille, Leroy & Hospital, 1972; Roberts, Petterson, Sheldrick, Isaacs & Kennard, 1973; Busetta, Courseille, Fornies-Marquina & Hospital, 1972; Courseille, Precigoux, Leroy & Busetta, 1973), it was considered worthwhile to attempt crystallization of the title compound in different solvents, hopefully to

obtain a new crystal form. Crystals obtained from ethanol solution were found to belong to a new crystalline modification. The X-ray crystallographic results of this form are presented here and the conformational flexibility of the title compound in two independent crystal environments is discussed.

Experimental. Colourless needles crystallized from saturated solution in ethanol kept at 273 K in the refrigerator. Unit-cell parameters in this paper differ from those reported by Precigoux *et al.* (1975). Cell parameters determined accurately on Nonius CAD-4 diffractometer by least-squares analysis of 25 reflections with $2\theta \geq 30^\circ$. Intensity data collected on Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed 1° min^{-1} . Crystal dimensions $0.2 \times 0.3 \times 0.5$ mm approx. Intensity variation monitored by frequently remeasuring 111 and 112, which varied only within 5%. 3136 reflections (including controls) measured (max. $2\theta = 45^\circ$; $h - 11 \rightarrow 11$, $k 0 \rightarrow 13$, $l 0 \rightarrow 16$), 2158 considered observed [$|F_o| \geq 3\sigma(F_o)$]. No absorption correction. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement for anisotropic O and C and isotropic H atoms using $w = [\sigma(|F_o|)^2 + 0.002|F_o|^2]^{-1}$, final $R = 0.060$ ($R_w = 0.065$), $S = 1.79$. $\sum w(|F_o| - |kF_c|)^2$ minimized using *SHELX76* (Sheldrick, 1976). Δ/σ for nonhydrogen atoms ~ 0.01 . Final difference Fourier map featureless. Atomic scattering factors of *SHELX* used.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond angles, H-bonding parameters and intermolecular contacts < 3.5 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39577 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.