Belicchi Ferrari, Gasparri Fava & Pellinghelli, 1973) mais cependant est très significatif du déplacement de la contrainte stérique du cycle à cinq sur le cycle à quatre atomes.

Dans le même sens, l'atome d'azote du groupe amide est fortement pyramidal: écart de 0,8 Å de l'azote au dessus du plan moyen des trois substituants. Cette déformation est encore la résultante de l'importante tension due à la fusion des deux cycles.

### Références

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Belicchi Ferrari, M., Gasparri Fava, G. & Pellinghelli, M. A. (1973). *Cryst. Struct. Commun.* **2**, 511–514.

Gramain, J. C., Dufour, M., Ouazzani-Chahadi, L., Remuson, R. & Troin, Y. (1981). X$^e$ Conf. Int. Photochem., Heraklion.

Gramain, J. C., Ouazzani-Chahadi, L. & Troin, Y. (1981). *Tetrahedron Lett.* pp. 3185–3188.

*International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

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. de York, Angleterre, et Louvain-la-Neuve, Belgique.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. A Program for Drawing Crystal and Molecular Structures.* Univ. de Cambridge, Angleterre.

---

*Acta Cryst.* (1985). C**41**, 1095–1100

# Cycloaddition of Isoquinolinium-*N*-phenylimide with Dimethyl Fumarate and Dimethyl Maleate and their Acid Rearrangement Products: $C_{21}H_{20}N_2O_4$ (6) and $C_{24}H_{22}N_2O_6$ (7)

By Isabella L. Karle and Judith L. Flippen-Anderson

*Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC* 20375–5000, *USA*

and Rolf Huisgen

*Institut für Organische Chemie der Universität München,* 8000 *München* 2, *Federal Republic of Germany*

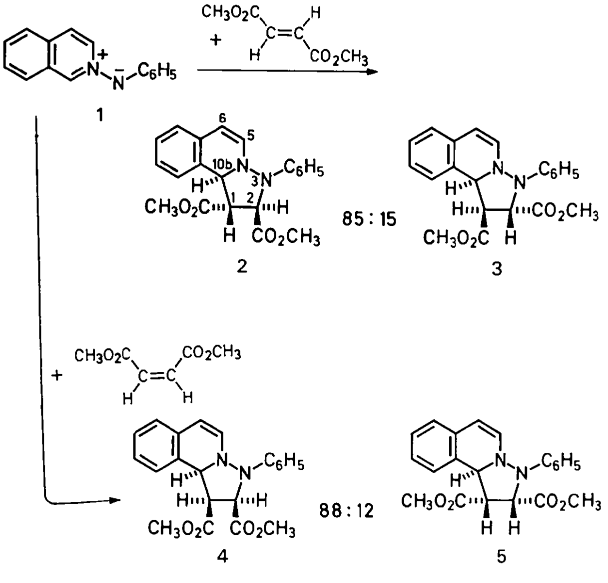
(*Received* 9 *October* 1984; *accepted* 20 *March* 1985)

**Abstract.** (6): $C_{21}H_{20}N_2O_4.0{\cdot}167H_2O.0{\cdot}083CH_3OH$, $M_r = 364{\cdot}43 + \sim 6$, triclinic, $P\bar{1}$, $a = 12{\cdot}121$ (4), $b = 17{\cdot}280$ (6), $c = 11{\cdot}612$ (4) Å, $\alpha = 91{\cdot}2$ (1), $\beta = 129{\cdot}8$ (2), $\gamma = 94{\cdot}6$ (1)°, $V = 1854{\cdot}2$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}33$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 7{\cdot}8$ cm$^{-1}$, $F(000) = 781$, room temperature, $R = 10{\cdot}8\%$ for 5270 unique reflections (all data within $2\theta = 126{\cdot}5°$). The two molecules per asymmetric unit of the fused pentacyclic product from the acid-catalyzed isomerization of the cycloaddition product from isoquinolinium-*N*-phenylimide and dimethyl fumarate are nearly identical. They are products of a hydrazo rearrangement and represent an intermediate stage of the Fischer indole synthesis. For an arbitrarily chosen hand, the new compound is: dimethyl (5*S*,6a*R*,7*R*,11b*S*,12*R*,13*R*)-5,6,6a,11b-tetrahydro-5,7-ethano-7*H*-indolo[2,3-*c*]isoquinoline-12,13-dicarboxylate (IUPAC recommendation). In the fused pentacyclic moiety, the six-membered rings *A* and *E* are planar, the six-membered ring *B* has a chair conformation, while the six-membered ring *C* that contains the two nitrogen atoms has a boat conformation. There is a *cis* junction at the fusion of ring *B* with the five-membered ring *D*. Both ester moieties are attached to ring *C*. The solvent molecules near special positions are necessarily disordered and occur only at partial occupancy. (7): $C_{24}H_{22}N_2O_6$, $M_r = 434{\cdot}25$, triclinic, $P\bar{1}$, $a = 10{\cdot}728$ (1), $b = 13{\cdot}126$ (2), $c = 8{\cdot}788$ (1) Å, $\alpha = 96{\cdot}34$ (1), $\beta = 113{\cdot}03$ (1), $\gamma = 103{\cdot}45$ (1)°, $V = 1079{\cdot}2$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}337$ g cm$^{-3}$, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 8{\cdot}2$ cm$^{-1}$, $F(000) = 456$, room temperature, $R = 6{\cdot}2\%$ for 2816 unique reflections (all data within $2\theta = 112°$). The structural formula and relative stereoconfiguration of the compound resulting from the acid-treated cycloaddition product of isoquinolinium-*N*-phenylimide and dimethyl maleate have been established by crystal structure analysis. Acid treatment of the cycloaddition product from isoquinolinium-*N*-phenylimide and dimethyl maleate (4) does not cause isomerization as in (6) above, but, rather, a deep-seated interaction of two molecules results in the abstraction of two hydrogen atoms from the pyrazolidine ring and the introduction of a $-CH_2CO_2CH_3$ side chain *meta* to the N atom in the isoquinoline moiety. The new compound (7) is (*S*)-6-(carboxymethyl)-2,3-dihydro-3-phenylpyrazolo-[5,1-*a*]isoquinoline-1,2-dicarboxylic acid, trimethyl ester (for an arbitrarily chosen hand). The tricyclic moiety along

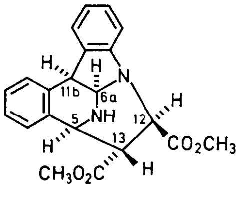
0108-2701/85/071095-06$01.50

with the ester on C(1) are essentially coplanar. The phenyl group on the tetrahedral N(3) is anti *gauche* with respect to the ester moiety on C(2).

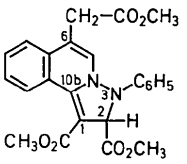
**Introduction.** The reaction of isoquinolinium-*N*-phenylimide (1), a 1,3-dipole, with dimethyl fumarate furnished an 85:15 mixture of the two cycloadducts (2)* and (3) quantitatively (Durst, 1965; Lindner, 1977; Temme, 1980); *trans*-located ester groups in (2) and (3) establish the retention of dipolarophile configuration. Analogously, the combination of the 1,3-dipole (1) with dimethyl maleate afforded the diastereoisomeric *cis* diesters (4) and (5). The stereospecific course is in harmony with the concerted nature of the cycloaddition process (Huisgen, 1983).



Short refluxing of (2) with picric acid in methanol gave 80% of the picrate of an isomeric base that contains a *sec*-amino group (Durst, 1965; Lindner, 1977). The $^1H$ NMR spectrum of the isomeric base $C_{21}H_{20}N_2O_4$ (m.p. 425–426 K) was in agreement with the pentacyclic structure (6). The separation of the nitrogen functions suggested a hydrazo rearrangement. The first step of Fischer's indole synthesis (Fischer & Hess, 1884) is in the acid-catalyzed tautomerization of a ketone phenylhydrazone to an ene-phenylhydrazine. Adduct (2) constitutes such an ene-phenylhydrazine, which smoothly undergoes the rearrangement according to the accepted mechanism (Robinson & Robinson, 1918), but stops at the intermediate stage (6) before the indolization takes place. Elimination of N(6) as an amino function would establish a double bond between C(6a) and C(11b) and thus provide an indole derivative. The occurrence of a *cis* and *trans* double bond in an eight-membered ring of this indole derivative would create ring strain of $> 80$ kJ mol$^{-1}$. This is probably the first example in which ring strain prohibits the final aromatization (Robinson, 1982). Our X-ray analysis confirmed structure (6) and, indirectly, secured the pathway *via* (2). The assignment of structures (2) and (3) to the major and minor cycloadduct was originally based on $^1H$ NMR arguments, which were not fully convincing. Furthermore, the X-ray analysis revealed that the six-membered ring containing the two nitrogen atoms unexpectedly occurs in a boat conformation.



6



7

The minor adduct (5), obtained from (1) + maleic acid ester, suffers a corresponding hydrazo rearrangement, which leads to a stereoisomer of (6). In contrast, the reaction of the main adduct (4) with HCl in dichloromethane took a fundamentally different course. The adduct $C_{21}H_{20}N_2O_4$ was converted to a yellow base $C_{24}H_{22}N_2O_6$ (Durst, 1965). The three additional C atoms form a side chain $-CH_2-CO_2CH_3$ and come from a second molecule of (4). On the basis of this stoichiometry the yield of $C_{24}H_{22}N_2O_6$ (m.p. 455–457 K) reached 85% (Temme, 1980). The X-ray analysis unveiled structure (7). It required several years to elucidate the mechanism of this reaction (Finke, 1984), which appears somewhat mysterious at first glance. The mechanism will be published elsewhere.

The relative stereoconfigurations of (6) and (7) shown in the figures in this paper were chosen arbitrarily since racemates of both molecules occur in the respective crystals.

**Experimental.** Crystal (6). Yellow prismatic crystals grown from methanol solution. Crystal size 0·4 × 0·1 × 0·05 mm. Picker FACS-I diffractometer, Cu $K\alpha$, $\theta/2\theta$ scan, $2\theta_{max} = 126·5°$, $-13 \le h \le 10$, $-15 \le k \le 15$, $0 \le l \le 12$; standard reflections 0,15,0, 700, 006 monitored every 100 measurements, variations of 4% in intensity; 12 reflections used for deriving lattice parameters; corrections for Lorentz and polarization effects, not for absorption. Since $Z = 4$ for a triclinic cell, the cell parameters were subjected to the procedure for obtaining the reduced cell and searching

---

* (2): Dimethyl (1*R*,2*R*,10b*S*)-1,2,3,10b-tetrahydro-3-phenylpyrazolo[5,1-*a*]isoquinoline-1,2-dicarboxylate.

(4): Dimethyl (1*S*,2*R*,10b*S*)-1,2,3,10b-tetrahydro-3-phenylpyrazolo[5,1-*a*]isoquinoline-1,2-dicarboxylate.

for additional symmetry (*International Tables for X-ray Crystallography,* 1969; Mighell & Rodgers, 1980). There was no indication of higher symmetry. Structure solved by direct method of phase determination using the symbolic addition procedure (Karle & Karle, 1966). All 54 non-hydrogen atoms, representing the two molecules in the asymmetric unit, found in one $E$ map computed with 915 highest $|E|$ values. Least-squares refinement; difference map indicated positions for two solvent molecules, which must be disordered. These positions were interpreted as ~1/3 occupancy for both a molecule of $H_2O$ and a molecule of $CH_3OH$ with mutual exclusion.[*] Further description of disorder appears in *Discussion.* Full-matrix least-squares refinement on $|F|$. In the early stages of refinement, data were limited to reflections with $|F_o| > 4\cdot0$ (3513 reflections). Positions for all hydrogen atoms except three on methyl C(27) and one on methyl C(27*A*) located in difference map. Remaining four hydrogen atoms placed in idealized positions. Final cycle of least-squares refinement on 493 parameters calculated using all 5270 data with parameters for hydrogen atoms fixed. Weights according to Gilardi (1973). $R = 10\cdot8\%$ for all data,[†] $(\Delta/\sigma)_{\max} = 1\cdot0$, $(\Delta\rho)_{\max} = +0\cdot68$, $(\Delta\rho)_{\min} = -0\cdot71$ e Å$^{-3}$. Coordinates for non-hydrogen atoms and approximate coordinates for solvent molecules are listed in Table 1. Selected torsion angles are in Table 2 and bond lengths and bond angles are shown in Figs. 1(*a*) and 1(*b*).

Crystal (7). Yellow thin diamond-shaped plates grown from a mixture of chloroform and ether. Crystal size 0·35 × 0·50 × 0·03 mm. Nicolet *P*3 diffractometer, Cu $K\alpha$, $\theta/2\theta$ scan, $2\theta_{\max} = 112°$, $-11 \le h \le 10$, $-14 \le k \le 13$, $0 \le l \le 9$; standard reflections 800, $\bar{1}$,12,0, $\bar{1}\bar{1}8$, variations of 4% in intensity; 12 reflections used in deriving cell parameters; corrections for Lorentz and polarization effects, not for absorption. Structure solved by deriving phases with symbolic addition procedure. Positions for 19 of 22 hydrogen atoms found in difference map after least-squares refinement of non-hydrogen atoms. Two hydrogen atoms on C(23) and one hydrogen on C(12) placed in idealized positions. Full-matrix anisotropic least-squares refinement on $F$ of 32 C, N and O atoms (H-atom parameters fixed) resulted in $R$ 6·2% for all 2816 data (no unobserved reflections).[†] Weights according to Gilardi (1973), $wR = 6\cdot6\%$, $S = 0\cdot96$, $(\Delta/\sigma)_{\max} = 0\cdot3$, $(\Delta\rho)_{\max} = +0\cdot25$, $(\Delta\rho)_{\min} = -0\cdot35$ e Å$^{-3}$. Coordinates for non-hydrogen atoms are listed in Table 3 and bond lengths and bond angles are shown in Fig. 2.

Computer programs used included *ORXFLS*3 (Busing *et al.,* 1975), *ORTEP* (Johnson, 1965) and in-house programs for data reduction, phase determination and tangent formula refinement and expansion. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Coordinates and $B_{eq}$ values for the two molecules of* (6) *in the asymmetric unit*

Standard deviations are given in parentheses

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$)* |
|---|---|---|---|---|
| Molecule (I) | | | | |
| C(1) | 0·9805 (6) | 0·8919 (4) | 0·6201 (6) | 2·5 (1) |
| C(2) | 0·9271 (7) | 0·8173 (4) | 0·5078 (7) | 2·7 (1) |
| C(3) | 1·0065 (6) | 0·8148 (3) | 0·4476 (6) | 2·2 (1) |
| C(4) | 0·9603 (7) | 0·8541 (4) | 0·3230 (7) | 2·8 (1) |
| C(5) | 1·0290 (7) | 0·8494 (4) | 0·2627 (7) | 3·5 (2) |
| C(6) | 1·1434 (8) | 0·8070 (4) | 0·3266 (8) | 3·7 (2) |
| C(7) | 1·1929 (7) | 0·7696 (4) | 0·4560 (7) | 3·3 (2) |
| C(8) | 1·1251 (6) | 0·7739 (3) | 0·5175 (6) | 2·2 (1) |
| C(9) | 1·1878 (6) | 0·7341 (3) | 0·6625 (6) | 1·6 (1) |
| C(10) | 1·3281 (7) | 0·7854 (4) | 0·7913 (6) | 2·6 (1) |
| C(11) | 1·4628 (7) | 0·7898 (4) | 0·8322 (7) | 3·3 (2) |
| C(12) | 1·5737 (8) | 0·8437 (5) | 0·9480 (8) | 3·8 (3) |
| C(13) | 1·5454 (8) | 0·8952 (4) | 1·0202 (8) | 3·6 (2) |
| C(14) | 1·4077 (7) | 0·8903 (4) | 0·9810 (7) | 2·7 (1) |
| C(15) | 1·3006 (6) | 0·8343 (3) | 0·8664 (6) | 2·3 (1) |
| N(16) | 1·1594 (6) | 0·8127 (3) | 0·8164 (5) | 2·6 (2) |
| C(17) | 1·0565 (6) | 0·8670 (4) | 0·7777 (6) | 2·6 (1) |
| N(18) | 0·9436 (6) | 0·7451 (3) | 0·5808 (6) | 3·1 (2) |
| C(19) | 1·0931 (7) | 0·7402 (4) | 0·7077 (7) | 3·1 (2) |
| C(20) | 1·1255 (7) | 0·9368 (4) | 0·8947 (7) | 3·0 (2) |
| O(21) | 1·1525 (5) | 1·0014 (3) | 0·8778 (5) | 3·5 (3) |
| O(22) | 1·1537 (6) | 0·9163 (3) | 1·0206 (5) | 4·8 (3) |
| C(23) | 1·2247 (9) | 0·9787 (5) | 1·1437 (9) | 5·6 (3) |
| C(24) | 0·8589 (7) | 0·9360 (4) | 0·5712 (7) | 2·9 (2) |
| O(25) | 0·8112 (5) | 0·9419 (3) | 0·6351 (6) | 4·8 (3) |
| O(26) | 0·8041 (5) | 0·9693 (3) | 0·4424 (5) | 3·8 (3) |
| C(27) | 0·6843 (8) | 1·0141 (5) | 0·3851 (8) | 4·7 (4) |
| Molecule (II) | | | | |
| C(1*A*) | 0·4705 (6) | 0·4796 (3) | 0·6848 (6) | 0·9 (1) |
| C(2*A*) | 0·3598 (6) | 0·4033 (3) | 0·6268 (6) | 2·4 (1) |
| C(3*A*) | 0·3936 (6) | 0·3361 (4) | 0·5709 (6) | 1·3 (1) |
| C(4*A*) | 0·3401 (7) | 0·3270 (4) | 0·4226 (7) | 2·9 (2) |
| C(5*A*) | 0·3643 (7) | 0·2629 (4) | 0·3725 (7) | 3·5 (2) |
| C(6*A*) | 0·4416 (8) | 0·2064 (4) | 0·4696 (8) | 3·7 (2) |
| C(7*A*) | 0·4970 (8) | 0·2164 (4) | 0·6174 (8) | 3·2 (1) |
| C(8*A*) | 0·4774 (7) | 0·2823 (4) | 0·6724 (7) | 2·8 (1) |
| C(9*A*) | 0·5538 (6) | 0·2966 (3) | 0·8371 (6) | 3·0 (1) |
| C(10*A*) | 0·7104 (6) | 0·3281 (4) | 0·9245 (6) | 2·6 (1) |
| C(11*A*) | 0·8214 (7) | 0·2900 (4) | 0·9535 (7) | 3·0 (2) |
| C(12*A*) | 0·9571 (7) | 0·3321 (4) | 1·0319 (7) | 3·6 (2) |
| C(13*A*) | 0·9819 (7) | 0·4091 (4) | 1·0799 (8) | 3·5 (2) |
| C(14*A*) | 0·8728 (7) | 0·4482 (4) | 1·0534 (7) | 3·1 (2) |
| C(15*A*) | 0·7345 (6) | 0·4058 (4) | 0·9720 (6) | 2·4 (1) |
| N(16*A*) | 0·6105 (5) | 0·4329 (3) | 0·9407 (5) | 2·4 (1) |
| C(17*A*) | 0·5490 (6) | 0·5004 (4) | 0·8514 (6) | 1·2 (1) |
| N(18*A*) | 0·3558 (5) | 0·3781 (3) | 0·7426 (6) | 2·7 (1) |
| C(19*A*) | 0·4969 (7) | 0·3619 (4) | 0·8739 (7) | 2·9 (2) |
| C(20*A*) | 0·6636 (6) | 0·5701 (4) | 0·9136 (6) | 2·5 (2) |
| O(21*A*) | 0·7081 (5) | 0·5950 (3) | 0·8538 (5) | 3·7 (2) |
| O(22*A*) | 0·7115 (5) | 0·5992 (3) | 1·0492 (5) | 3·7 (3) |
| C(23*A*) | 0·8223 (9) | 0·6663 (5) | 1·1204 (9) | 5·1 (4) |
| C(24*A*) | 0·3911 (6) | 0·5462 (4) | 0·5952 (6) | 2·6 (1) |
| O(25*A*) | 0·3709 (6) | 0·6013 (3) | 0·6394 (5) | 4·3 (3) |
| O(26*A*) | 0·3379 (5) | 0·5328 (2) | 0·4526 (5) | 3·2 (2) |
| C(27*A*) | 0·2535 (8) | 0·5928 (4) | 0·3530 (8) | 3·6 (2) |
| Solvent | | | | $B_{iso}$(Å$^2$) |
| *M*–C | 0·0000 | 0·5000 | 0·5000 | 7·7 |
| *M*–O | 0·0478 (4) | 0·4285 (2) | 0·5634 (5) | 3·0 (8) |
| $H_2O$ | 0·1973 (2) | 0·5207 (1) | 0·7114 (2) | 8·9 (4) |

* $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

---

[*] The crystal is no longer available for an experimental density measurement.

[†] Lists of observed and calculated structure factors, anisotropic thermal parameters and approximate hydrogen coordinates for (6) and (7) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42128 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected torsion angles for* (6) (°)

The e.s.d.'s are near 0·9°.

| | Molecule (I) | Molecule (II) |
|---|---|---|
| Ring *B* | | |
| C(2)C(3)C(8)C(9) | −4 | −11 |
| C(3)C(8)C(9)C(19) | 5 | 16 |
| C(8)C(9)C(19)N(18) | 28 | 18 |
| C(9)C(19)N(18)C(2) | −64 | −60 |
| C(19)N(18)C(2)C(3) | 63 | 66 |
| N(18)C(2)C(3)C(8) | −28 | −29 |
| Ring *C* | | |
| C(1)C(2)N(18)C(19) | −62 | −59 |
| C(2)N(18)C(19)N(16) | 54 | 59 |
| N(18)C(19)N(16)C(17) | 6 | −2 |
| C(19)N(16)C(17)C(1) | −57 | −53 |
| N(16)C(17)C(1)C(2) | 47 | 51 |
| C(17)C(1)C(2)N(18) | 9 | 4 |
| Ring *D* | | |
| C(9)C(10)C(15)N(16) | 9 | 6 |
| C(10)C(15)N(16)C(19) | 4 | 4 |
| C(15)N(16)C(19)C(9) | −16 | −12 |
| N(16)C(19)C(9)C(10) | 20 | 15 |
| C(19)C(9)C(10)C(15) | −18 | −14 |

**Discussion.** (6). The acid-catalyzed isomerization of (2) to (6) involves a hydrazo rearrangement as described in the *Introduction*. The two independent molecules of (6) in the asymmetric unit are quite similar in all respects. One of the molecules is shown in Fig. 3. The six-membered rings *A* and *E* are essentially planar, with the average absolute values for the ring torsion angles being 1·6 (9) and 2·1 (9)° for ring *A* in the two molecules and 1·7 (9) and 0·8 (9)° for ring *E*. The six-membered ring *B* has an envelope conformation with N(18) 0·70 (4) Å out of the plane of the other five ring atoms in both molecules. Six-membered ring *C* has a boat conformation with C(17) and N(18) each being 0·60 (5) Å out of the plane formed by the other four atoms in both molecules. There is a *cis* junction at the fusion of rings *B* and *D*. The five-membered ring *D* is twisted about the C(9)—C(19) bond such that the two atoms are staggered above and below the plane formed by C(10), C(15) and N(16). The two methyl ester moieties are *gauche* with respect to one another, with the C(24)C(1)C(17)C(20) torsion angle equal to 63·0 (9)° in both molecules.

Even though the two molecules in the asymmetric unit are nearly identical, the environment in the crystal around each is different. The nearest approaches between equivalent atoms in molecules (I) and (II) are almost all different, for example, the distance N(16)-(I)···C(11)(II) ($2-x$, $1-y$, $2-z$) is 3·13 (5) Å, whereas the distance N(16)(II)···C(11)(I) [where N(16)(II) is at $2-x$, $1-y$, $2-z$] is greater than 4·0 Å. Furthermore, the solvent that has co-crystallized occupies sites only between molecules (I) and (II), but not between molecule (I) and its symmetry equivalent or between molecule (II) and its symmetry equivalent.

Water and $CH_3OH$ cocrystallize as solvent molecules with partial occupancy. The C atom of the methanol molecule occurs on a center of symmetry (0, $\frac{1}{2}$, $\frac{1}{2}$). If the space group is indeed centrosymmetric, then the OH group must be disordered between two positions. The $H_2O$ molecule forms a weak hydrogen bond with O(25)(II) at 2·98 Å and a stronger one with one of the disordered methanol hydroxyls ($\bar{x}$, $1-y$, $1-z$) at 2·86 Å. However, the $H_2O$ molecule cannot coexist

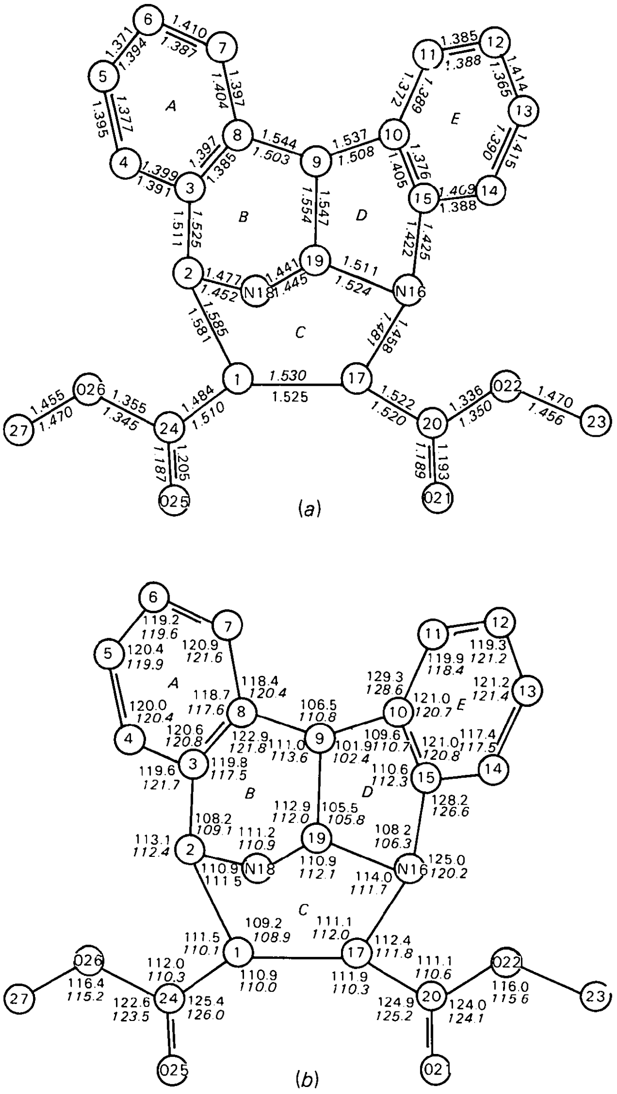


Fig. 1. (*a*) Bond lengths (Å) for the two molecules in the asymmetric unit of (6). The values in roman type are for molecule (I) and those in italic type for molecule (II). Standard deviations are of the order of 0·006 Å. Note that the numbering in Fig. 1 is used for the crystal structure and is different from the numbering used in formula (6) and in the nomenclature. (*b*) Bond angles (°) for the two molecules in the asymmetric unit of (6). The values in roman type are for molecule (I) and those in italic type for molecule (II). Standard deviations are of the order of 0·6°.

Table 3. *Coordinates and $B_{eq}$ values for* (7)

Standard deviations are near 0·0004, 0·0003 and 0·0004 for $x$, $y$ and $z$, respectively

| | $x$ | $y$ | $z$ | $B_{\text{eq}}$(Å$^2$)* |
|---|---|---|---|---|
| C(1) | 0·2418 | 0·1865 | 0·3780 | 3·2 |
| C(2) | 0·1433 | 0·1555 | 0·4621 | 3·2 |
| N(3) | 0·0782 | 0·2450 | 0·4588 | 3·1 |
| N(4) | 0·1683 | 0·3288 | 0·4247 | 3·0 |
| C(5) | 0·1637 | 0·4311 | 0·4537 | 3·2 |
| C(6) | 0·2417 | 0·5082 | 0·4109 | 3·2 |
| C(6a) | 0·3300 | 0·4800 | 0·3352 | 3·0 |
| C(7) | 0·4120 | 0·5569 | 0·2832 | 3·8 |
| C(8) | 0·4965 | 0·5296 | 0·2129 | 4·1 |
| C(9) | 0·5037 | 0·4244 | 0·1901 | 4·1 |
| C(10) | 0·4265 | 0·3461 | 0·2402 | 3·6 |
| C(10a) | 0·3388 | 0·3736 | 0·3141 | 3·0 |
| C(10b) | 0·2562 | 0·2920 | 0·3675 | 3·0 |
| C(11) | 0·3043 | 0·1113 | 0·3333 | 4·1 |
| C(12) | 0·3014 | −0·0733 | 0·3096 | 8·3 |
| C(13) | 0·2215 | 0·1535 | 0·6488 | 3·9 |
| C(14) | 0·1836 | 0·1010 | 0·8821 | 6·3 |
| C(15) | −0·0699 | 0·2166 | 0·3360 | 3·3 |
| C(16) | −0·1663 | 0·1443 | 0·3730 | 4·2 |
| C(17) | −0·3098 | 0·1163 | 0·2658 | 5·1 |
| C(18) | −0·3574 | 0·1600 | 0·1261 | 5·4 |
| C(19) | −0·2615 | 0·2318 | 0·0904 | 5·1 |
| C(20) | −0·1156 | 0·2606 | 0·1964 | 4·2 |
| C(22) | 0·2285 | 0·6207 | 0·4383 | 3·9 |
| C(22) | 0·1132 | 0·6308 | 0·2781 | 4·2 |
| C(23) | −0·1379 | 0·5902 | 0·1229 | 8·8 |
| O(1) | 0·3910 | 0·1232 | 0·2751 | 6·6 |
| O(2) | 0·2533 | 0·0144 | 0·3618 | 5·3 |
| O(3) | 0·3455 | 0·1913 | 0·7366 | 6·4 |
| O(4) | 0·1276 | 0·1050 | 0·7037 | 4·7 |
| O(5) | 0·1307 | 0·6626 | 0·1645 | 7·7 |
| O(6) | −0·0136 | 0·5936 | 0·2755 | 5·7 |

* $B_{\text{eq}} = \frac{4}{3}\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j$.

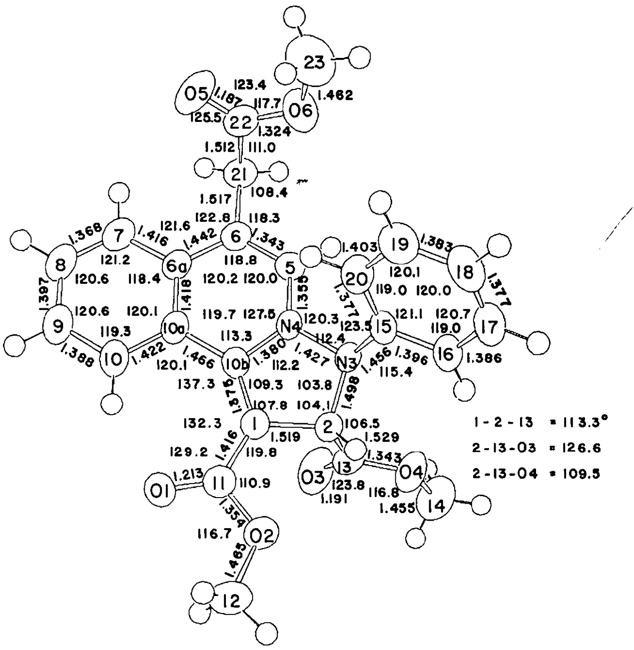


Fig. 2. Bond lengths (Å) and bond angles (°) for (7). E.s.d.'s for the bond lengths are of the order of 0·006 Å, and for the bond angles they are near 0·4°.

in any unit cell containing the alternate position for the methanol hydroxyl since their intermolecular separation would be only 2·0 Å. The alternate methanol hydroxyl ($x$, $y$, $z$) is involved in a weak hydrogen bond with N(18)(II) at 3·12 Å. There is no possibility of any hydrogen-bond formation with N(18)(I) since this atom is effectively shielded by atoms C(2), C(3) and C(4) from molecule (II). The only other close intermolecular approach found in the cell is N(18)(II)···O(22)(II) ($1-x$, $1-y$, $2-z$) at 3·0 Å, but not N(18)(I)···O(22)(I).

(7). The acid-catalyzed reaction of (4) to (7) involved an abstraction of two H atoms from C(1) and C(10b), which resulted in a double bond between these two atoms, and, more curiously, involved the replacement of an H atom on C(6) with a $-CH_2COOCH_3$ group. The latter group is derived from the decomposition of another molecule of (4) *via* a complex reaction sequence.

The tricyclic moiety in (7), Figs. 2 and 4, is essentially coplanar along with atoms C(11) and C(21). The largest deviation from a least-squares plane through the 15 atoms is 0·22 (2) Å for N(3), while the

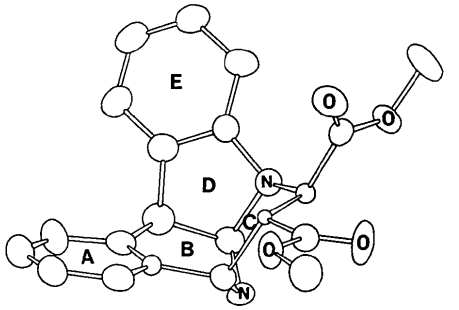


Fig. 3. Diagram of the results of the X-ray analysis of (6) drawn with program *ORTEP* (Johnson, 1965). Only one of the two similar molecules in the asymmetric unit is shown in an arbitrarily chosen hand.

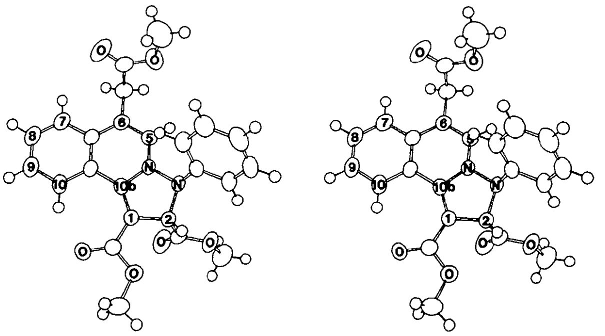


Fig. 4. Stereodiagram of (7). The hand has been chosen arbitrarily since the molecules occur as racemates in the crystal.

mean deviation is 0·06 (1) Å. Atoms C(2) and N(3) are tetrahedral and their substituents, *i.e.* the carboxyl methyl ester and the phenyl group, respectively, are anti *gauche* to each other with the torsional angle C(13)-C(2)N(3)C(15) equal to −133 (1)°. The remaining carboxyl methyl ester on C(6) is tilted to the same side of the molecule as the phenyl group. The torsional angle C(5)C(6)C(21)C(22) is equal to −91 (1)°. Bond lengths and angles have expected values except, perhaps, in the five-membered ring, Fig. 2.

There are no solvent molecules in the crystal and no possible hydrogen bonds. The isoquinolyl moieties in adjacent molecules related by a center of symmetry at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ stack over each other. The parallel planes are separated by only 3·35 (2) Å. Atoms C(6), C(7), C(9) and C(10a) of one molecule lie directly over C(9′), C(10a′), C(6′) and C(7′), respectively, of the other molecule, where the intermolecular distances C(6)···C(9′) and C(7)···C(10a′) are 3·35 (2) Å. Atoms C(6a) and C(8) of one molecule lie over the centers of the rings of the isoquinolyl moiety of the other molecule. Distances between atoms C(6a) and C(8) to atoms in the antiparallel isoquinoline range between 3·53 (2) and 3·63 (2) Å.

## References

Busing, W. R., Martin, K. O., Levy, H. A., Ellison, R. D., Hamilton, W. C., Ibers, J. A., Johnson, C. K. & Thiessen, W. E. (1975). *ORXFLS*3. Oak Ridge National Laboratory, Tennessee.

Durst, T. (1965). Univ. of Munich. Unpublished.

Finke, J. (1984). Univ. of Munich. Unpublished.

Fischer, E. & Hess, O. (1884). *Ber. Dtsch. Chem. Ges.* **17**, 559–568.

Gilardi, R. D. (1973). *Acta Cryst.* B**29**, 2089–2095.

Huisgen, R. (1983). 1,3-*Dipolar Cycloaddition Chemistry*, edited by A. Padwa, Vol. 1, pp. 35–52, 61–76. New York: John Wiley.

*International Tables for X-ray Crystallography* (1969). Vol. I, 3rd ed., pp. 530–535: reduced-cell section by A. D. Mighell, A. Santoro & J. D. H. Donnay. Birmingham: Kynoch Press.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Lindner, K. (1977). Univ. of Munich. Unpublished.

Mighell, A. D. & Rodgers, J. R. (1980). *Acta Cryst.* A**36**, 321–326.

Robinson, B. (1982). *The Fischer Indole Synthesis*. New York: John Wiley.

Robinson, G. M. & Robinson, R. (1918). *J. Chem. Soc.* **113**, 639–645.

Temme, R. (1980). Univ. of Munich. Unpublished.

---

*Acta Cryst.* (1985). C**41**, 1100–1104

# Azido-2 Désoxy-2 β-D-Galactopyrannoside Méthylique, $C_7H_{13}N_3O_5$, et Azido-2 Désoxy-2 β-D-Galactopyrannoside Ethylique, $C_8H_{15}N_3O_5$

PAR N. DARBON, Y. ODDON, E. GUY, B. FERRARI ET A. A. PAVIA

*Laboratoire de Chimie Bioorganique, UER des Sciences,* 33 *rue Louis Pasteur,* 84000 *Avignon, France*

G. PÈPE

*Centre de Recherche sur les Mécanismes de la Croissance Cristalline, Université d'Aix-Marseille III, Campus Luminy, Case* 913, 13288 *Marseille CEDEX* 2, *France*

ET J. P. REBOUL

*Laboratoire de Chimie Thérapeutique, Faculté de Pharmacie, Université d'Aix-Marseille II,* 27 *boulevard Jean Moulin,* 13385 *Marseille CEDEX* 5, *France*

(*Reçu le* 16 *juillet* 1984, *accepté le* 20 *mars* 1985)

**Abstract.** $C_7H_{13}N_3O_5$: $M_r = 219{\cdot}2$, monoclinic, $C2$, $a = 16{\cdot}630$ (4), $b = 8{\cdot}866$ (3), $c = 6{\cdot}924$ (3) Å, $\beta = 97{\cdot}57$ (2)°, $V = 1011{\cdot}9$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}439$, $D_m = 1{\cdot}45$ (1) Mg m$^{-3}$, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\bar{\alpha}) = 0{\cdot}08$ mm$^{-1}$, $F(000) = 464$, $T = 293$ K, final $R = 0{\cdot}038$ for 1002 independent reflections. $C_8H_{15}N_3O_5$: $M_r = 233{\cdot}2$, orthorhombic, $P22_12_1$, $a = 4{\cdot}670$ (2), $b = 6{\cdot}933$ (2), $c = 34{\cdot}941$ (9) Å, $V = 1131{\cdot}3$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}370$, $D_m = 1{\cdot}36$ (1) Mg m$^{-3}$, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\bar{\alpha}) = 0{\cdot}07$ mm$^{-1}$, $F(000) = 496$, $T = 293$ K, final $R = 0{\cdot}046$ for 699 independent reflections. The conformation of the hydroxyl group O(6)—H(O6) about C(5)—C(6) is '*trans–gauche*' and the pyranose ring exists in the normal chair ($^4C_1$) conformation. In both crystals, molecules are associated by hydrogen bonds. C—OCH$_3$ [1·358 (11) Å] in the

0108-2701/85/071100-05$01.50