Table 4. *Systematic deformation of sp^2 angles in the O-methoxybenzamide fragment shown in Fig. 3, listed together with relevant torsion angles; p-substituted anisoles (average value) and benzamide values are reported for comparison (e.s.d.'s, when available, $0·6°$)*

φ	χ	ψ	τ_1	τ_2	τ_3	Reference
117·0°	126·7°	119·4°	−177·6°	−13·7°	−6·1°	(1)
116·7	126·2	119·2	−175·4	−4·8	0·9	(2)
116·7	126·2	119·4	174·4	−16·9	−3·5	(3)
117	125	119	169·1	13·0	*	(4)
117	127	118	*	*	*	(5)
117	128	116	176·5	11·1/−13·9 |molecules (1)/(2)|		(6)
117·5	125·5	119·2	−176·7	4·1	6·8	(7)
117·8	126·0	117·7	−177·1	−6·3	0·0	(8)
115	—	—	176·5	—	—	(9)
—	121·7	117·5	—	−27·8	−17·8,−173·4 (two H atoms)	(10)

References: (1) BPDDM (1980): primperan. (2) BPDDM (1981): sulpiride hydrochloride. (3) BPDDM (1982): tiapride hydrochloride. (4) Houttemane, Boivin, Nowogrocki, Thomas & Bonte (1981): racemic sulpiride. (5) Ma, Camerman & Camerman (1982): racemic sulpiride. (6) Ma, Camerman & Camerman (1982): $S(-)$-sulpiride average [molecules (1) and (2)]. (7) This paper. (8) Foresti, Riva di Sanseverino & Sabatino, unpublished. (9) Di Rienzo, Domenicano, Portalone & Vaciago (1976): p-substituted anisoles. (10) Blake & Small (1972): benzamide.
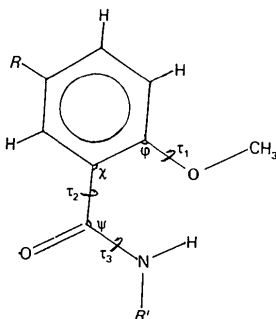
* Coordinates unavailable for calculations.

Fig. 3. The o-methoxybenzamide fragment with relevant angles labelled as in Table 4.

References

BLAKE, C. C. F. & SMALL, R. W. H. (1972). *Acta Cryst.* B28, 2201–2206.

BLATON, N. M., PEETERS, O. M., DE RANTER, C. J., DENISOFF, O. & MOLLE, L. (1980). *Cryst. Struct. Commun.* 9, 857–864.

BLATON, N. M., PEETERS, O. M., DE RANTER, C. J., DENISOFF, O. & MOLLE, L. (1981). *Cryst. Struct. Commun.* 10, 833–838.

BLATON, N. M., PEETERS, O. M., DE RANTER, C. J., DENISOFF, O. & MOLLE, L. (1982). *Cryst. Struct. Commun.* 11, 1357–1362.

DE CUNTO, M., BERRETTINI, M., PARISE, P., DE REGIS, M., ORZALESI, G. & NENCI, G. G. (1983). *Boll. Soc. Ital. Biol. Sper.* 59, 302–308.

DI RIENZO, F., DOMENICANO, A. & FORESTI SERANTONI, E. (1977). *Acta Cryst.* B33, 3854–3858.

DI RIENZO, F., DOMENICANO, A., PORTALONE, G. & VACIAGO, A. (1976). *Proc. Yugosl. Cent. Crystallogr.* 11, A102–A104.

DOMIANO, P., NARDELLI, M., BALSAMO, A., MACCHIA, B. & MACCHIA, F. (1979). *Acta Cryst.* B35, 1363–1372.

HALFPENNY, J. & SMALL, R. W. H. (1980a). *Acta Cryst.* B36, 1194–1196.

HALFPENNY, J. & SMALL, R. W. H. (1980b). *Acta Cryst.* B36, 2786–2788.

HERBSTEIN, F. H., KAFTORY, M., KAPON, M. & SAENGER, W. (1981). *Z. Kristallogr.* 154, 11–30.

HOUTTEMANE, C., BOIVIN, J. C., NOWOGROCKI, G., THOMAS, D. J. & BONTE, J. P. (1981). *Acta Cryst.* B37, 981–984.

KATO, Y. & SAKURAI, K. (1982). *Bull. Chem. Soc. Jpn*, 55, 1643–1644.

LEISEROWITZ, L. & TUVAL, M. (1978). *Acta Cryst.* B34, 1230–1247.

MA, L. Y. Y., CAMERMAN, N. & CAMERMAN, A. (1982). *Acta Cryst.* B38, 2861–2865.

MOTHERWELL, W. D. S. (1976). *PLUTO*. A program for drawing crystal and molecular structures. Univ. of Cambridge, England.

ROBERTS, P. J. & SHELDRICK, G. M. (1975). *XANADU*. A program for crystallographic calculations. Univ. of Cambridge, England.

SAKURAI, K. (1982). *Mem. Osaka Kyoiku Univ.* 30, 119–136.

SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

TANIGUCHI, T., NAKATA, K., TAKAKI, Y. & SAKURAI, K. (1978). *Acta Cryst.* B34, 2574–2578.

Structure of 5,11-Methano-2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[b,f][1,5]diazocine (Tröger's Base) at 163 K

BY S. B. LARSON AND C. S. WILCOX

Department of Chemistry, University of Texas at Austin, Austin, TX 78712, USA

Abstract. $C_{17}H_{18}N_2$, $M_r = 250·34$, orthorhombic, *Pccn*, $a = 12·774$ (2), $b = 30·290$ (5), $c = 10·386$ (2) Å, $V = 4018·5$ (13) Å^3, $Z = 12$, $D_x = 1·241$, $D_m = 1·20$ (1) g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0·71069$ Å, $\mu = 0·685$ cm^{-1}, $F(000) = 1608$, $T = 163$ K, $R = 0·0668$ for 1738 reflections, $(F \geq 4\sigma_F)$. There are 1·5 molecules per

asymmetric unit. Eight molecules per cell, related by the general positions 'e', have only approximate C_2 symmetry while four molecules per cell possess exact C_2 symmetry lying on special positions 'd'. The intramolecular dihedral angle between the planes of the aromatic rings is 92·85 (17) and 97·38 (16)°, respectively, for the two independent molecules.

Introduction. The title compound, first prepared by Tröger (1887), has an interesting history and over the past 100 years has been studied by a number of workers. The structural formula was in dispute for several decades. The correct connectivity was established by Spielman (1935). This amine is chiral, and the resolution of the base into its enantiomeric forms was first accomplished by Prelog & Wieland (1944). It is interesting to note that this was the first amine, chiral solely due to the difficulty of inversion at N, to be resolved. Investigations into the mechanism of formation of this base were carried out by Wagner and co-workers (Eisner & Wagner, 1934; Wagner, 1937, 1954; Miller & Wagner, 1938, 1941) and by Farrar (1964). Greenberg, Molinaro & Lang (1984) have investigated the mechanism of the acid-catalyzed racemization of the amine.

Our interest in this molecule was stimulated by the fact that Tröger's base and analogous dibenzodiazocines are easily prepared and relatively rigid chiral synthetic structural units and could be used to good advantage in the synthesis of biomimetic molecular systems of interest to us. The rational use of Tröger's-base analogs for the preparation of biomimetic systems requires a detailed knowledge of the three-dimensional structure of the parent system. The dihedral angle formed by the two planes which include the aromatic rings was of particular interest. We report here on the structure of the racemic mixture.

Experimental. Tröger's base prepared from toluidine and formaldehyde by method of Goecke (1903). Suitable crystals for analysis were prepared by sublimation at 398 K [0·4 mmHg (0·5 × 10² Pa)]; m.p. 403–404 K. Data crystal cut from a thin needle perpendicular to needle axis (c axis). Summary of data collection and structural refinement given in Table 1.

Structure solved by $MULTAN78$ (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier techniques and refined by full-matrix least squares ($SHELX76$, Sheldrick, 1976); all atomic positional parameters refined as well as anisotropic thermal parameters for non-hydrogen atoms and isotropic for H atoms. Electron density difference map calculated at $R = 0·11$ revealed all non-methyl H atoms and two sets of H atoms for each methyl C atom; each methyl treated as two idealized rigid groups. Occupancies for H atoms refined to: 0·59:0·41 for C(16); 0·51:0·49 for C(17); and 0·74:0·26 for C(16T). The

Table 1. *Crystallographic summary for* $C_{17}H_{18}N_2$

(*a*) Data collection (163 K)*†

Mode	ω scan
Scan range	Symmetrically over 1·0° about $K\alpha_{1,2}$ maximum
Background	Offset 0·75° and −0·75° in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min⁻¹)	2·0–5·0
Exposure time (h)	72·7
Stability analysis†	
Computed s	0·00013 (14)
t	−0·000000 (2)
Correction range (on I)	0·990–1·000
2θ range (°)	4·0–50·0
Range in hkl, min.	0,0,0
max.	15,36,12
Total reflections measured	3538
Crystal volume (mm³)	0·0130
Crystal faces, dimensions (mm)	{010}, 0·14; {100}, 0·15; (0$\bar{1}\bar{1}$), (001), 0·60
Absorption, transmission-factor range	0·990–0·991

(*b*) Structure refinement‡

Instability factor p‡	0·02
Reflections used, m ($F > 4\sigma_F$)	1738
No. of variables, n	352
Extinction parameter§	0·00016 (5)
Goodness of fit, S	1·464
R, wR	0·0668, 0·0499
R for all data	0·156
Max. shift/e.s.d.	0·46 [C(17)_y rotation – oscillates +/−]
Max., min. in difference map (e Å⁻³)	0·30, −0·29

* Unit-cell parameters obtained by least-squares refinement of the setting angles of 43 reflections with 12·2° < 2θ < 22·0°. Crystal density measured by flotation in aqueous ZnCl₂.

† Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N₂) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by re-measurement of 4 check reflections after every 96 reflections. As detailed by Henslee & Davis (1975), these data were analyzed to relate intensity to exposure time by the equation $y = 1·0 + sx + tx^2$ where x is exposure time (h), y is fractional intensity relative to $x = 0$ and s and t are coefficients determined by least-squares fit.

‡ Function minimized was $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$; $\sigma_F = F\sigma_I/2I$; $\sigma_I = [N_{pk} + N_{bg1} + N_{bg2} + (pI)^2]^{1/2}$.

§ Extinction parameter x in expression $F^* = F(1 - 0·0001xF^2/\sin\theta)$.

large values of R result from having to use a very small crystal that diffracted poorly (especially for $2\theta > 35°$) as suggested by the number of unobserved reflections. Scattering factors and anomalous-dispersion corrections for all non-H atoms taken from *International Tables for X-ray Crystallography* (1974); H scattering factors from Stewart, Davidson & Simpson (1965). Principal computer programs are given by Gadol & Davis (1982); program for least-squares-planes calculations from Cordes (1983). Atomic parameters are in Table 2.*

Discussion. Fig. 1 illustrates the atom labeling of the molecule in general positions (referred to as molecule G but not indicated in labeling). Molecule T lies around a crystallographic twofold axis [atom C(15T) lies on the

* Tables of H parameters, anisotropic thermal parameters, hydrogen-bond lengths and angles, torsion angles, least-squares planes and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42514 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positions as fractional coordinates and* U_{eq} *for non-hydrogen atoms in* $C_{17}H_{18}N_2$

$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct-space unit-cell vectors.

	x	y	z	$U_{eq}(\text{Å}^2)$
N(1)	0·1515 (3)	0·48468 (13)	0·2570 (4)	0·0265 (14)
N(2)	0·3287 (3)	0·45661 (13)	0·2344 (4)	0·0274 (14)
C(1)	0·1918 (4)	0·5177 (2)	0·3435 (5)	0·024 (2)
C(2)	0·1208 (4)	0·5434 (2)	0·4145 (5)	0·033 (2)
C(3)	0·1563 (5)	0·5742 (2)	0·5009 (5)	0·031 (2)
C(4)	0·2640 (4)	0·5820 (2)	0·5187 (5)	0·029 (2)
C(5)	0·3320 (4)	0·5572 (2)	0·4467 (5)	0·029 (2)
C(6)	0·2987 (4)	0·52473 (15)	0·3600 (5)	0·025 (2)
C(7)	0·3764 (4)	0·4964 (2)	0·2875 (6)	0·034 (2)
C(8)	0·3052 (4)	0·4241 (2)	0·3317 (5)	0·028 (2)
C(9)	0·3866 (4)	0·3994 (2)	0·3835 (5)	0·032 (2)
C(10)	0·3671 (5)	0·3680 (2)	0·4766 (6)	0·039 (2)
C(11)	0·2662 (4)	0·3597 (2)	0·5204 (5)	0·030 (2)
C(12)	0·1856 (4)	0·3843 (2)	0·4684 (5)	0·027 (2)
C(13)	0·2029 (4)	0·4169 (2)	0·3744 (5)	0·028 (2)
C(14)	0·1142 (4)	0·4457 (2)	0·3242 (5)	0·031 (2)
C(15)	0·2333 (4)	0·4704 (2)	0·1670 (5)	0·030 (2)
C(16)	0·3002 (4)	0·6141 (2)	0·6202 (5)	0·038 (2)
C(17)	0·2452 (5)	0·3262 (2)	0·6244 (5)	0·044 (2)
N(1T)	0·2265 (3)	0·78868 (13)	0·4724 (4)	0·029 (2)
C(1T)	0·1456 (4)	0·7786 (2)	0·3800 (5)	0·027 (2)
C(2T)	0·0945 (4)	0·8137 (2)	0·3180 (5)	0·030 (2)
C(3T)	0·0143 (4)	0·8052 (2)	0·2322 (5)	0·033 (2)
C(4T)	−0·0174 (4)	0·7622 (2)	0·2060 (4)	0·032 (2)
C(5T)	0·0345 (4)	0·7278 (2)	0·2658 (5)	0·029 (2)
C(6T)	0·1165 (4)	0·7353 (2)	0·3521 (5)	0·028 (2)
C(7T)	0·1757 (4)	0·6970 (2)	0·4116 (6)	0·032 (2)
C(15T)	0·25	0·75	0·5487 (7)	0·033 (3)
C(16T)	−0·1036 (4)	0·7532 (2)	0·1096 (5)	0·048 (2)

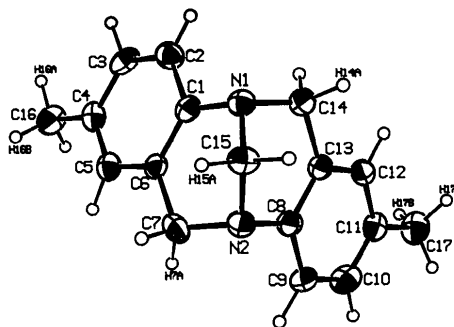
Fig. 1. View of title compound illustrating atom labeling. Thermal ellipsoids scaled to 50% probability.

Table 3. *Bond lengths* (Å) *and bond angles* (°) *in* $C_{17}H_{18}N_2$

1	2	3	1—2	1—2—3
Molecule G				
C(1)	N(1)	C(14)	1·439 (6)	112·5 (4)
C(14)	N(1)	C(15)	1·451 (7)	107·5 (4)
C(15)	N(1)	C(1)	1·467 (7)	110·3 (4)
C(7)	N(2)	C(8)	1·458 (7)	112·7 (4)
C(8)	N(2)	C(15)	1·443 (6)	110·9 (4)
C(15)	N(2)	C(7)	1·467 (7)	107·0 (4)
C(2)	C(1)	C(6)	1·405 (7)	118·9 (4)
C(2)	C(1)	N(1)		118·7 (4)
C(6)	C(1)	N(1)	1·393 (7)	122·3 (4)
C(3)	C(2)	C(1)	1·373 (7)	120·5 (5)
C(4)	C(3)	C(2)	1·408 (8)	121·5 (5)
C(5)	C(4)	C(16)	1·369 (7)	122·8 (5)
C(5)	C(4)	C(3)		117·1 (5)
C(16)	C(4)	C(3)	1·508 (7)	119·9 (5)
C(6)	C(5)	C(4)	1·400 (7)	123·0 (5)
C(7)	C(6)	C(1)	1·513 (8)	119·6 (4)
C(7)	C(6)	C(5)		121·4 (5)
C(1)	C(6)	C(5)		119·0 (5)
N(2)	C(7)	C(6)		112·6 (4)
C(9)	C(8)	C(13)	1·389 (7)	119·7 (5)
C(9)	C(8)	N(2)		118·8 (4)
C(13)	C(8)	N(2)	1·397 (7)	121·5 (4)
C(10)	C(9)	C(8)	1·381 (8)	120·5 (5)
C(11)	C(10)	C(9)	1·390 (8)	121·4 (5)
C(12)	C(11)	C(17)	1·380 (7)	120·8 (5)
C(12)	C(11)	C(10)		117·8 (5)
C(17)	C(11)	C(10)	1·506 (7)	121·4 (5)
C(13)	C(12)	C(11)	1·408 (7)	122·3 (5)
C(14)	C(13)	C(8)	1·521 (7)	119·9 (4)
C(14)	C(13)	C(12)		121·6 (5)
C(8)	C(13)	C(12)		118·4 (5)
N(1)	C(14)	C(13)		112·7 (4)
N(1)	C(15)	N(2)		111·8 (4)
Molecule T				
C(1T)	N(1T)	C(15T)	1·443 (6)	109·9 (3)
C(7T)*	N(1T)	C(1T)	1·466 (7)	112·7 (4)
C(15T)	N(1T)	C(7T)*	1·446 (6)	107·4 (3)
C(2T)	C(1T)	C(6T)	1·405 (7)	119·5 (4)
C(2T)	C(1T)	N(1T)		118·5 (4)
C(6T)	C(1T)	N(1T)	1·394 (7)	122·0 (4)
C(3T)	C(2T)	C(1T)	1·381 (7)	119·9 (5)
C(4T)	C(3T)	C(2T)	1·390 (8)	121·1 (5)
C(5T)	C(4T)	C(16T)	1·383 (7)	120·6 (5)
C(5T)	C(4T)	C(3T)		118·5 (5)
C(16T)	C(4T)	C(3T)	1·514 (7)	120·8 (5)
C(6T)	C(5T)	C(4T)	1·396 (7)	121·8 (5)
C(7T)	C(6T)	C(1T)	1·516 (7)	120·1 (4)
C(7T)	C(6T)	C(5T)		120·8 (4)
C(1T)	C(6T)	C(5T)		119·1 (5)
N(1T)	C(15T)	N(1T)*		113·6 (5)

* Atoms transformed by $\frac{1}{2}-x, \frac{1}{2}-y, z$.

axis] and is labeled to correspond to molecule G. Bond lengths and bond angles (Table 3) are normal. There is very good agreement in bond lengths and angles involving chemically equivalent atoms in the three unique but chemically equivalent C_9H_9N moieties comprising the asymmetric unit.

The intramolecular dihedral angle between the least-squares planes through the aromatic rings is 92·85 (17)° for molecule G and 97·38 (16)° for molecule T. The intramolecular inter-methyl distance is 8·751 (7) and 9·037 (8) Å for G and T respectively. The nearly 90° bend in the molecule is illustrated with the side view of molecule G in Fig. 2 which also illustrates the packing of a unit cell. Molecules of T are seen in end-on view.

Molecules of both G and T stack like spoons in the c direction. Closest contacts in this direction are H(15)A···C(6) 2·67 (4), H(15)B···C(12) 2·73 (5), and H(15T)···C(5T) 2·81 (4) Å. That these H atoms are directed toward the center of the aromatic rings is suggested by the spread in the H(15) to ring C distances |2·67 (4)–2·80 (4) Å, for H(15)A; 2·73 (5)–2·96 (5) Å for H(15)B; and 2·81 (4)–3·12 (4) Å for H(15T)|. Between the independent molecules, the closest distances are N(1T) to H(16)B1 and H(16)B2 |a pair of disordered H atoms on C(16)|. These are 2·754 (6) and 2·396 (6) Å respectively.
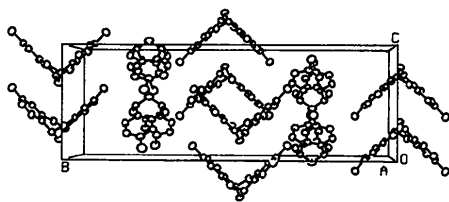
Fig. 2. Molecular packing diagram as viewed down the *a* axis. The eight molecules of *G* are viewed approximately along the folding axis whereas the four molecules of *T* are viewed perpendicular to the folding axis.

References

CORDES, A. W. (1983). Personal communication.

EISNER, A. & WAGNER, E. C. (1934). J. Am. Chem. Soc. 56, 1938–1943.

FARRAR, W. V. (1964). J. Appl. Chem. 14, 389–399.

GADOL, S. M. & DAVIS, R. E. (1982). Organometallics, 1, 1607–1613.

GOECKE, G. (1903). Z. Elektrochem. 9, 470–473.

GREENBERG, A., MOLINARO, N. & LANG, M. (1984). J. Org. Chem. 49, 1127–1134.

HENSLEE, W. H. & DAVIS, R. E. (1975). Acta Cryst. B31, 1511–1519.

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

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MILLER, T. R. & WAGNER, E. C. (1938). J. Am. Chem. Soc. 60, 1738–1741.

MILLER, T. R. & WAGNER, E. C. (1941). J. Am. Chem. Soc. 63, 832–836.

PRELOG, V. & WIELAND, P. (1944). Helv. Chim. Acta, 27, 1127–1134.

RILEY, P. E. & DAVIS, R. E. (1976). Acta Cryst. B32, 381–386.

SHELDRICK, G. M. (1976). SHELX76. A crystallographic computing package. Univ. of Cambridge, England.

SPIELMAN, M. A. (1935). J. Am. Chem. Soc. 57, 583–585.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

TRÖGER, J. (1887). J. Prakt. Chem. 36, 225–245.

WAGNER, E. C. (1937). J. Org. Chem. 2, 157–166.

WAGNER, E. C. (1954). J. Org. Chem. 19, 1862–1881.

Diphényl-2,5 Dipyrazinyl-3,4 Pyrrole Ethanol Monohydrate

PAR B. VIOSSAT

Laboratoire de Chimie Minérale, UER de Médecine et de Pharmacie, 34 rue du Jardin des Plantes, 86034 Poitiers CEDEX, France

N. RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, rue J.-B. Clément, 92290 Châtenay-Malabry, France

ET J. LEHUEDE ET J.-M. VIERFOND

Laboratoire de Chimie Organique, UER de Médecine et de Pharmacie, 34 rue du Jardin des Plantes, 86034 Poitiers CEDEX, France

Abstract. $C_{24}H_{17}N_5.C_2H_6O.H_2O$, $M_r = 439.5$, monoclinic, $P2_1/c$, $a = 18.751$ (8), $b = 8.493$ (2), $c = 14.896$ (8) Å, $\beta = 93.06$ (4)°, $V = 2369$ (2) Å³, $Z = 4$, $D_x = 1.232$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 7.53$ mm⁻¹, $F(000) = 928$, $T = 295$ (2) K, $R = 0.050$ for 1840 independent observed reflections. The ethanol molecule occupies, in statistical disorder, four positions. In the molecule of 2,5-diphenyl-3,4-dipyrazinylpyrrole, interatomic distances and bond angles are in good agreement with previously published values. The five rings are planar. Hydrogen bonds O—H⋯N, N—H⋯O and O—H⋯O take part in the cohesion of the structure.

Introduction. Les essais de cyclisation de l'amino-1 phényl-1 pyrazinyl-2 éthylène conduisent à un produit inattendu dont l'étude par les méthodes spectrographiques habituelles (masse, IR, RMN de ¹H et de ¹³C) n'a pas permis de déterminer la structure moléculaire. Par exemple, les spectres de RMN révèlent seulement la présence de protons (ou d'atomes de carbone) aromatiques et d'un proton échangeable par