and X-ray structure analysis respectively. These values are all less than the angle of 121·7° reported for bicyclobutane (Cox, Harmony, Nelson & Wiberg, 1969, 1970). Although the C(2)—C(10) bond distance and the above dihedral angle in (3) do not conform to the precise relationship described in the literature, their values are consistent with the highly strained nature of this heterocyclic system.

References

BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–435.

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* 10, 180–182.

CHIANG, J. F. (1971). *J. Am. Chem. Soc.* 93, 5044–5047.

CHRISTL, M. & HERZOG, C. (1986). *Chem. Ber.* 119, 3067–3075.

CHRISTL, M. & KRAFT, A. (1988). *Angew. Chem. Int. Ed. Engl.* 27, 1369–1370.

COX, K. W., HARMONY, M. D., NELSON, G. & WIBERG, K. B. (1969). *J. Chem. Phys.* 50, 1976–1980.

COX, K. W., HARMONY, M. D., NELSON, G. & WIBERG, K. B. (1970). *J. Chem. Phys.* 53, 858.

DEROSKI, B. R., MARKGRAF, J. H. & RICCI, J. S. (1983). *J. Heterocycl. Chem.* 20, 1155–1158.

DEROSKI, B. R., RICCI, J. S. JR, MACBRIDE, J. A. H. & MARK-GRAF, J. H. (1984). *Can. J. Chem.* 62, 2235–2237.

HULL, R., MACBRIDE J. A. H. & WRIGHT, P. M. (1984). *J. Chem. Res.* (*S*), pp. 328–329.

IRNGARTINGER, H. & LUKAS, K. L. (1979). *Angew. Chem. Int. Ed. Engl.* 18, 694–695.

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

MCMULLAN, R. K. (1979). A differential synthesis crystal structure refinement program. Unpublished.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.- P. & WOOLFSON, M. M. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARKGRAF, J. H., MUELLER, T. & MYERS, C. R. (1989). *Heterocycles,* 29, 2399–2402.

MARKGRAF, J. H. & SCOTT, W. L. (1967). *J. Chem. Soc. Chem. Commun.* pp. 296–297.

MOOMAW, W. R., KLEIER, D. A., MARKGRAF, J. H., THOMAN, J. W. JR & RIDYARD, J. N. A. (1988). *J. Phys. Chem.* 92, 4892–4898.

PADDON-ROW, M. N., HOUK, K. N., DOWD, P., GARNER, P. & SCHAPPERT, R. (1981). *Tetrahedron Lett.* 22, 4799–4802.

SHIRO, M. (1988). Personal communication to JHM.

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

SUENRAM, R. D. & HARMONY, M. D. (1973). *J. Am. Chem. Soc.* 95, 4506–4511.

TANIDA, H., IRIE, T. & HAYASHI, Y. (1984). *J. Org. Chem.* 49, 2527–2533.

ZEBELMAN, D. L., BAUER, S. H. & CHIANG, J. F. (1972). *Tetrahedron,* 28, 2727–2740.

ZIL'BERG, S. P., IOFFE, A. I. & NEFEDOV, O. M. (1983). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 255–260.

Structure of 2-Phenyl-1,2,3-triazolo[4,5-*e*][1,2,3,4]tetrazine at 153 K

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Abstract. $C_8H_5N_7$, $M_r = 199·2$, monoclinic, $P2_1/n$, $a = 14·780$ (3), $b = 5·325$ (2), $c = 10·805$ (3) Å, $\beta = 95·59$ (2)°, $U = 846·3$ (5) Å^3, $Z = 4$, $D_x = 1·563$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1·5405$ Å, $\mu = 0·927$ mm^{-1}, $F(000) = 408$, $T = 153$ K, final $R = 0·069$ for 794 observed reflections. The triazolotetrazine ring is planar indicating extensive π-electron delocalization. The C—C bond length in this ring [1·383 (9) Å] indicates a significant deviation from the estimation based on semiempirical MO calculations. The dihedral angle between this ring and the phenyl ring is 1·4 (6)°.

Introduction. We have previously described the first example of an aromatic 1,2,3,4-tetrazine (Kaihoh, Itoh, Yamaguchi & Ohsawa, 1988). Although previous analysis established the structure of this compound, crystal instability at room temperature did not provide a satisfactory basis for detailed discussion. The present paper describes an X-ray-diffraction study of the title compound at 153 K and will make a contribution to the theoretical studies of the unknown 1,2,3,4-tetrazine ring system.

Experimental. The preparation and physical properties of this compound are given in Kaihoh *et al.* (1988). An explosive reddish plate, 0·09 × 0·02 × 0·38 mm, by recrystallization from tetrahydrofuran at 253 K. Rigaku AFC5 four-circle diffractometer used with ω–2θ scan method, ω-scan width (1·3 + 0·41tanθ)°, scan speed 16° min^{-1}. Lattice parameters obtained from least-squares analysis of 23 reflections

with 2θ values ranging from 21 to 49°. Out of 1520 reflections scanned within index range h $-16{\rightarrow}16$, k $0{\rightarrow}6$, l $0{\rightarrow}12$ up to $\sin\theta/\lambda \le 0\cdot56$ Å^{-1} including 82 equivalent reflections ($R_{int} = 0\cdot09$), 1250 unique reflections $[F > \sigma(F)]$ classified as observed. Three standard reflections measured every 150 reflections, intensity variation < 3%. Intensities corrected for Lorentz and polarization factors, but absorption correction not applied. Structure solved using the *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985) version of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors for non-H atoms. The function minimized was $\Sigma w[(|F_o|)^2 - (|F_c|)^2|]^2$ with $w = 1/[\sigma^2(F_o) + 0\cdot028(F_o)^2]$, $\sigma(F_o)$ determined from counting statistics. All H atoms located from theoretical calculations were refined, initial thermal parameters set at equivalent isotropic thermal parameter of each bonded atom. Final discrepancy indices $R = 0\cdot069$, $wR = 0\cdot067$, $S = 1\cdot361$ for 794 reflections with $F > 3\sigma(F)$. Maximum $\Delta/\sigma = 0\cdot10$ in final least-squares cycle. Final difference Fourier excursions $0\cdot36$ and $-0\cdot32$ e Å^{-3}. All major computations performed on PANAFACOM computer with the *RCRYSTAN* (Rigaku Corporation, 1985) X-ray analysis program system. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are listed in Table 1.* The bond lengths and angles are listed in Table 2. Fig. 1 shows the thermal-ellipsoid plot of the molecule.

The triazolotetrazine ring system is almost planar, with maximum displacement out of the least-squares plane of $0\cdot017$ Å for C(9). This planarity and the endocyclic bond distances including the ring-junction [C(8)—C(9)] bond distance of $1\cdot383$ (9) Å indicate an extensive delocalization of π-electron density. How-

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and least-squares planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53273 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
N(1)	0·1482 (3)	−0·3048 (8)	0·8089 (5)	3·18 (16)
N(2)	0·1970 (3)	−0·4126 (9)	0·7274 (5)	3·66 (17)
N(3)	0·1973 (3)	−0·3258 (9)	0·6063 (5)	3·72 (19)
N(4)	0·1500 (3)	−0·1263 (8)	0·5643 (4)	3·32 (16)
N(5)	0·0436 (3)	0·1795 (8)	0·6279 (4)	2·91 (16)
N(6)	0·0134 (3)	0·2003 (8)	0·7412 (4)	2·54 (14)
N(7)	0·0445 (3)	0·0380 (7)	0·8294 (4)	2·91 (15)
C(8)	0·0995 (4)	−0·0161 (10)	0·6473 (5)	2·63 (18)
C(9)	0·1003 (4)	−0·1045 (9)	0·7677 (5)	2·53 (17)
C(10)	−0·0516 (3)	0·3912 (10)	0·7667 (5)	2·62 (18)
C(11)	−0·0803 (4)	0·5550 (10)	0·6734 (5)	2·58 (18)
C(12)	−0·1409 (4)	0·7415 (11)	0·7002 (6)	3·34 (22)
C(13)	−0·1729 (4)	0·7583 (11)	0·8184 (6)	3·14 (21)
C(14)	−0·1421 (4)	0·5837 (13)	0·9075 (6)	3·64 (22)
C(15)	−0·0818 (4)	0·3967 (11)	0·8841 (5)	2·96 (20)

Table 2. *Bond lengths* (Å) *and angles* (°)

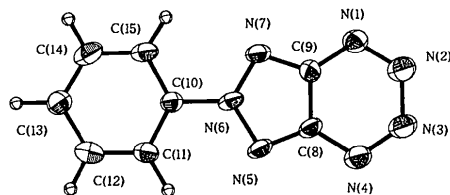|			
N(1)—N(2)	1·323 (8)	N(6)—C(10)	1·444 (7)
N(1)—C(9)	1·332 (7)	N(7)—C(9)	1·344 (8)
N(2)—N(3)	1·388 (8)	C(10)—C(11)	1·369 (8)
N(3)—N(4)	1·328 (7)	C(11)—C(12)	1·387 (9)
N(4)—C(8)	1·354 (8)	C(12)—C(13)	1·408 (10)
C(8)—C(9)	1·383 (9)	C(13)—C(14)	1·383 (9)
C(8)—N(5)	1·334 (7)	C(14)—C(15)	1·377 (10)
N(5)—N(6)	1·348 (7)	C(15)—C(10)	1·385 (9)
N(6)—N(7)	1·335 (6)		
N(1)—N(2)—N(3)	122·3 (4)	N(6)—C(10)—C(11)	118·2 (5)
N(2)—N(3)—N(4)	122·6 (5)	N(6)—C(10)—C(15)	117·9 (5)
N(3)—N(4)—C(8)	115·2 (5)	C(10)—C(11)—C(12)	117·6 (6)
N(4)—C(8)—N(5)	127·3 (5)	C(11)—C(12)—C(13)	121·0 (5)
N(4)—C(8)—C(9)	121·3 (5)	C(12)—C(13)—C(14)	118·2 (6)
C(8)—N(5)—N(6)	100·1 (4)	C(13)—C(14)—C(15)	122·2 (6)
N(5)—N(6)—N(7)	118·3 (4)	C(14)—C(15)—C(10)	117·0 (5)
N(5)—N(6)—C(10)	121·9 (4)	C(15)—C(10)—C(11)	123·8 (5)
N(6)—N(7)—C(9)	101·3 (4)		
N(7)—C(9)—N(1)	128·1 (5)		
N(7)—C(9)—C(8)	108·9 (5)		
C(9)—N(1)—N(2)	115·5 (5)		
C(8)—C(9)—N(1)	122·8 (6)		
N(7)—N(6)—C(10)	120·6 (4)		
N(5)—C(8)—C(9)	111·2 (5)		

Fig. 1. Thermal-ellipsoid plot. Ellipsoids are drawn at the 50% probability level while isotropic hydrogen thermal parameters are represented by spheres of arbitrary size.

ever, the semiempirical molecular-orbital calculations using *AM*1 methods (Dewar, Zoebisch, Hearly & Stewart, 1985) indicated a single-bond character in the C(8)—C(9) distance of $1\cdot5008$–$1\cdot5012$ Å. This difference is probably due to unsuitable estimation in the *AM*1 parameters concerning the nuclear repulsion factor for this type of electron-deficient ring system containing many N atoms. This tendency is also observed in the similar compound 2-phenyl-1,2,3-triazolo[4,5-*b*]pyrazine (Yamaguchi, Ohsawa & Kawabata, 1990) which has an identical ring system except that N(2) and N(3) are both substituted by CH [observed C—C length of $1\cdot393$ (6) and calculated value of $1\cdot5003$ Å]. The bond parameters of triazolopyrazine derived from X-ray analysis are in good agreement with triazolotetrazine except for the angles N(2)—N(1)—C(9) and N(3)—N(4)—C(8) [115·5 (5) and 115·2 (5)° in triazolotetrazine and corresponding C—N—C angles 111·8 (4) and 111·2 (3)°

in triazolopyrazine respectively]. The dihedral angle between triazolotetrazine and the phenyl ring is close to 0° [1·4 (6)°], indicating attractive interactions H(C11)···N(5) of 2·45 (5) Å [∠H(C11) = 97 (3)°] and H(C15)···N(7) of 2·43 (5) Å [∠H(C15) = 99 (4)°] (Taylor & Kennard, 1982) as well as the partial double-bond character between sp^2-hybridized N and C atoms [N(6)—C(10) distance is 1·444 (7) Å].

Intermolecular hydrogen bonds and unusual short non-bonded contacts are not observed.

References

DEWAR, M. J. S., ZOEBISCH, E. G., HEARLY, E. F. & STEWART, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

KAIHOH, T., ITOH, T., YAMAGUCHI, K. & OHSAWA, A. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1608–1609.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Rigaku Corporation (1985). *RCRYSTAN. X-ray Analysis Program System.* Rigaku Corporation, Tokyo, Japan.
TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
YAMAGUCHI, K., OHSAWA, A. & KAWABATA, C. (1990). *Acta Cryst.* C46, 1751–1752.
YAO, J.-X., ZHENG, C.-D., QIAN, J.-Z., HAN, F.-S., GU, Y.-X. & FAN, H.-F. (1985). *A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Institute of Physics, Academia Sinica, Beijing, People's Republic of China.

Structure of 3-Acetoxyindole

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Abstract. Indol-3-yl acetate, $C_{10}H_9NO_2$, $M_r = 175·2$, monoclinic, $P2_1/c$, $a = 6·777$ (2), $b = 8·706$ (3), $c = 15·375$ (4) Å, $\beta = 96·02$ (2)°, $V = 902·1$ (2) Å³, $Z = 4$, $D_m = 1·29$, $D_x = 1·290$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 0·850$ cm⁻¹, $F(000) = 368$, $T = 296$ K, $R = 0·065$ for 1117 observed reflections. The indole system and acetoxy group are almost planar, and the acetoxy group makes a dihedral angle of 66·1° with the pyrrole ring. The crystal structure is stabilized by an N—H···O hydrogen bond [N1—O2 = 2·849 (2) Å and ∠N1—H···O2 = 177°].

Introduction. The study of indole derivatives is important in the history of organic chemistry, due to their varied biological, chemical and pharmacological properties. The title compound is structurally similar to the important derivative, 3-indoleacetic acid which is a plant growth hormone. As an aid to understanding its biological and pharmacological significance, and to provide further structural data on substituted indoles, we have investigated the solid-state structure of the title compound by X-ray diffraction methods.

Experimental. Single crystals obtained by slow evaporation of the powdered substance in ether–petrol (1:3). The approximate dimensions of the selected specimen were 0·2 × 0·3 × 0·175 mm. Inten-

sities measured by ω–2θ scan method, $0 \le 2\theta \le 50°$, using a $P2_1$ diffractometer with Mo $K\alpha$ radiation. Density measured by flotation in aqueous KI solution. Unit-cell constants derived by least-squares analysis of 25 reflections for which $25° < 2\theta < 35°$. Range of h,k,l: $h = 0 \to 8$, $k = 0 \to 11$, $l = -19 \to 19$. Out of 1850 unique reflections, 1117 had intensities greater than $2\sigma(I)$ and were used in the subsequent analysis. Lorentz and polarization corrections were applied but no absorption or extinction corrections were made.

The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Refinement carried out first with isotropic temperature factors and then with anisotropic temperature factors for non-H atoms. H atoms associated with the benzene ring were generated geometrically. Other H atoms located from the difference map and given the same isotropic temperature factors as the atoms to which they were bonded. H-atom positions were not refined. The final $R = 0·065$ and $wR = 0·061$ with 118 parameters. $\sum w(\Delta F)^2$ minimized with weighting factor $w = 1/\sigma^2(F_o)$, S (goodness of fit) = 0·65, $(\Delta/\sigma)_{\text{max}} = 0·55$ and $(\Delta/\sigma)_{\text{mean}} = 0·31$. Maximum and minimum heights in final difference map were within $\pm 0·5$ e Å⁻³. The non-hydrogen scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and for H atoms from Stewart, Davidson & Simpson (1965).

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