

Table 1. Final atomic coordinates and B_{eq} values
$$B_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j B_{ij}$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
P	0.35958 (2)	0.44848 (6)	0.39159 (6)	1.410 (4)
O(1)	0.14910 (7)	0.6836 (2)	0.5956 (2)	2.09 (2)
O(2)	0.38837 (7)	0.5335 (2)	0.6411 (2)	2.09 (2)
O(3)	0.06530 (6)	-0.0022 (2)	0.7671 (2)	1.86 (2)
O(4)	0.23491 (6)	0.0512 (2)	0.6823 (2)	2.16 (2)
N	0.37437 (8)	0.9063 (2)	0.0060 (2)	2.01 (2)
C	0.04296 (9)	0.5176 (2)	0.0829 (2)	1.87 (2)

Table 2. Principal interatomic distances (\AA) and bond angles ($^\circ$) and details of the hydrogen-bonding scheme

PO_4 tetrahedron				
P	O(1)	O(2)	O(3)	O(4)
O(1)	1.574 (1)	2.521 (2)	2.467 (2)	2.524 (2)
O(2)	106.93 (6)	1.564 (1)	2.538 (1)	2.467 (1)
O(3)	106.58 (6)	111.74 (6)	1.503 (1)	2.524 (1)
O(4)	110.13 (6)	107.06 (6)	114.20 (6)	1.504 (1)

Min. P-P	4.130 (1)
P-O	1.536 (1)

 $\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3$ group

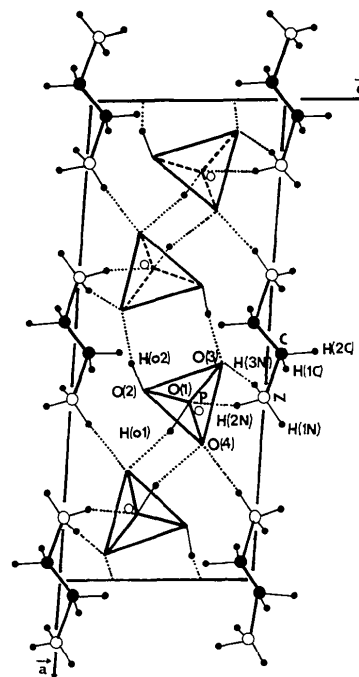
N-C	1.481 (2)
C-C	1.508 (3)
C-C-C	109.7 (1)

Hydrogen bonds

	(O,N)-H	H...O	(O,N)-O	(O,N)-H...O
O(1)-H(1)...O(4)	0.74 (2)	1.81 (2)	2.524 (2)	168 (2)
O(2)-H(2)...O(3)	0.74 (2)	1.83 (2)	2.538 (1)	177 (3)
N-H(1N)...O(4)	0.92 (2)	1.91 (2)	2.757 (2)	152 (2)
N-H(2N)...O(1)	0.83 (2)	2.08 (2)	2.892 (2)	163 (2)
N-H(3N)...O(3)	0.90 (2)	2.02 (2)	2.854 (2)	153 (2)

$(\text{H}_2\text{PO}_4)_n^{n-}$ chains belonging to two successive (002) planes.

All these hydrogen bonds (O-H...O and N-H...O types) give rise to a three-dimensional network in the structure and add stability to this compound.

Fig. 1. Projection along the b axis of the atomic arrangement of $\text{NH}_3-(\text{CH}_2)_2-\text{NH}_3 \cdot (\text{H}_2\text{PO}_4)_2$.

References

- AVERBUCH-POUCHOT, M. T. & DURIF, A. (1987). *Acta Cryst.* **C43**, 1894-1896.
- AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1987). *Acta Cryst.* **C43**, 1896-1898.
- Enraf-Nonius (1980). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- KAMOUN, S., JOUINI, A., KAMOUN, M. & DAOUD, A. (1988). *C.R. Acad. Sci.* To be submitted.

Acta Cryst. (1989). **C45**, 482-485

Structure of 1,4-Phenylenebis(3,3-diphenylketenimine)

BY WILMA KUIPERS, JAN A. KANTERS AND ARIE SCHOUTEN

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, 3584 CH Utrecht, The Netherlands

(Received 10 June 1988; accepted 4 October 1988)

Abstract. 1,4- N,N' -(2,2'-Diphenylvinylidene)phenylenediamine, $\text{C}_{34}\text{H}_{24}\text{N}_2$, $M_r = 460.58$, triclinic, $P\bar{1}$, $a = 7.928$ (7), $b = 9.474$ (6), $c = 9.599$ (4) \AA , $\alpha = 72.18$ (4), $\beta = 74.98$ (6), $\gamma = 68.84$ (6) $^\circ$, $V = 631.1$ (9) \AA^3 , $Z = 1$, $D_x = 1.212$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) =$

0.71073 \AA , $\mu = 0.7$ cm^{-1} , $F(000) = 242$, $T = 295$ K, final $R = 0.060$ for 1553 unique observed reflections. The compound is a centrosymmetric bisketenimine derivative. The ketenimine fragment has approximate C_s symmetry. The N -phenyl ring is nearly coplanar with

the two C=C=N fragments indicating conjugation of the phenyl and ketenimine π systems. The C=C=N chain deviates significantly from linearity; the angle is $171.5(3)^\circ$. The phenyl rings bonded to the C atom of the ketenimine fragment show different rotations with respect to the plane of the isopropylidene group, $46.2(2)$ and $18.7(2)^\circ$ respectively, thus minimizing steric repulsions between the aromatic H atoms.

Introduction. Ketanimines $R^1R^2C=C=NR^3$, in which R^1 , R^2 and R^3 are usually alkyl or aryl substituents, represent the class of heterocumulenes. X-ray results on ketanimines have revealed several interesting geometries (Runge, 1980; Jochims, Lambrecht, Burkert, Zsolnai & Huttner, 1984). The ketenimine fragment displays approximate C_s symmetry (Naqvi & Wheatley, 1970; Jochims *et al.*, 1984; Lambrecht, Gambke, von Seyerl, Huttner, Kollmannsberger-von Nell, Herzberger & Jochims, 1981). A remarkable feature is the deviation from linearity of the C=C=N chain which has been observed in all published structures of ketanimines.

Ketanimines have been industrially applied as chain-coupling agents in the preparation of polyethylene terephthalate (PET) (Sikkema, Molenaar & van Gulden, 1976). In order to study the properties of bisketanimines in relation to applications in polymer syntheses, the title compound was synthesized. The molecule consists of two 3,3-diphenylketenimine fragments which are coupled through a central phenyl ring. To elucidate the geometric and conformational details of this unusual bisketenimine derivative we undertook its structure analysis.

Experimental. Crystals were obtained from Akzo Research Laboratories, Arnhem, The Netherlands. A yellow, plate-shaped crystal of dimensions $0.15 \times 0.5 \times 0.7$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation. Lattice parameters were derived from the angular settings of 25 reflections with a θ range of 8.65 – 11.99° . Intensity statistics indicated space group $P\bar{1}$ which was confirmed by the results of the refinement. The intensity data of 2407 reflections were collected ($0 < h < 9$, $-11 < k < 11$, $-11 < l < 11$), with $2\theta_{\max} = 50^\circ$, ω - 2θ scan mode with $\Delta\omega = (0.60 + 0.35 \tan\theta)^\circ$, of which 1553 were above the $2.5\sigma(I)$ level. Two periodically measured standard reflections ($14\bar{1}$, $2\bar{2}1$) showed an r.m.s. deviation of 0.8%. The structure was solved by direct methods (SHELXS86; Sheldrick, 1986). H atoms on the terminal phenyl rings were placed at calculated positions (C–H 1.00 Å), the two H atoms on the central ring were located in a difference Fourier synthesis. In subsequent refinements the H atoms of the terminal phenyl rings were treated riding on their carrier atoms with a general isotropic temperature factor for each of the rings. In the final cycles of blocked full-matrix refinement on F^2

parameters were varied, including overall scale factor, positional and anisotropic thermal parameters of the non-H atoms and the positional parameters and a general isotropic temperature factor for the two H atoms at the central ring. The scattering factors for non-H atoms were taken from Cromer & Mann (1968), those for the H atoms from Stewart, Davidson & Simpson (1965). Calculations were performed with SHELX76 (refinement) (Sheldrick, 1976) and the EUCLID package (geometry calculations and illustrations) (Spek, 1982). The final R value was 0.060, $wR = 0.065$, $w = 3.2586[\sigma^2(F_o) + 0.000476(F_o)^2]^{-1}$, $S = 2.14$, $\langle \Delta/\sigma \rangle_{\text{av}} = 0.001$, $\langle \Delta/\sigma \rangle_{\text{max}} = 0.002$. The general isotropic temperature factors of the H atoms refined to $0.102(3)$, $0.093(4)$ and $0.074(3) \text{ \AA}^2$ respectively. Maximum and minimum residual density in the final difference map 0.22 and -0.27 e \AA^{-3} respectively.

Discussion. The final atomic coordinates and the equivalent isotropic thermal parameters are listed in Table 1. Bond distances, bond angles and selected torsion angles are given in Table 2.* A perspective view of the molecule with atom numbering is shown in Fig. 1.

The title compound consists of two diphenylketenimine fragments which are symmetrically connected by a central phenyl ring. As the centre of the molecule coincides with the centre of the space group (at $\frac{1}{2}, \frac{1}{2}, 0$), the asymmetric unit consists of one half molecule. The central and terminal groups are planar, the σ_{plane} values are 0.009, 0.006 and 0.008 \AA respectively. The central rigid part of the molecule consisting of the central phenyl ring and the two ketenimine chains, comprising 12 atoms, is nearly planar ($\sigma_{\text{plane}} = 0.035 \text{ \AA}$). The geometry of the ketenimine fragment is analogous to that of the allene skeleton, as follows from the C–C [$1.315(3) \text{ \AA}$] and C–N [$1.225(3) \text{ \AA}$] distances which indicate double bonds, the C=N–C and the two C=C angles which are $125.7(2)$, $117.2(2)$ and $119.7(2)^\circ$ respectively, and the angle of $88.0(3)^\circ$ between the isopropylidene and C=N–C planes which shows that the ketenimine fragment has approximate C_s symmetry. The complete molecule is distorted from C_s symmetry by the different twists of the terminal phenyl rings with respect to the isopropylidene plane, which are $46.2(2)$ and $18.7(2)^\circ$ respectively.

A scan through the Cambridge Crystallographic Database on the ketenimine fragment $R^1R^2C=C=NR^3$ (R^1 , R^2 and R^3 are alkyl or aryl substituents) resulted in ten hits in which the C=C and C=N distances average to $1.32(2)$ and $1.23(2) \text{ \AA}$ respectively and the C=

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51460 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	U_{eq}^*
N	0.3056 (3)	0.6392 (2)	0.2376 (2)	0.0602 (6)
C(1)	-0.0379 (4)	1.1236 (3)	0.3197 (3)	0.0630 (10)
C(2)	-0.0096 (5)	1.2658 (3)	0.2891 (4)	0.0830 (10)
C(3)	0.1029 (5)	1.3128 (4)	0.1608 (5)	0.0990 (20)
C(4)	0.1846 (5)	1.2191 (4)	0.0618 (4)	0.0960 (10)
C(5)	0.1556 (4)	1.0766 (3)	0.0924 (3)	0.0730 (10)
C(6)	0.0452 (3)	1.0278 (2)	0.2213 (3)	0.0538 (6)
C(7)	0.0197 (3)	0.8704 (2)	0.2572 (2)	0.0531 (6)
C(8)	-0.1607 (3)	0.8442 (2)	0.3122 (2)	0.0531 (8)
C(9)	-0.1726 (4)	0.6949 (3)	0.3818 (3)	0.0690 (10)
C(10)	-0.3379 (5)	0.6675 (4)	0.4286 (3)	0.0860 (10)
C(11)	-0.4960 (5)	0.7881 (4)	0.4087 (3)	0.0830 (10)
C(12)	-0.4888 (4)	0.9358 (4)	0.3418 (3)	0.0760 (10)
C(13)	-0.3224 (4)	0.9643 (3)	0.2936 (3)	0.0623 (8)
C(14)	0.1673 (3)	0.7522 (2)	0.2370 (3)	0.0571 (8)
C(15)	0.4019 (3)	0.5712 (2)	0.1142 (3)	0.0538 (6)
C(16)	0.3383 (3)	0.6199 (3)	-0.0191 (3)	0.0637 (8)
C(17)	0.5598 (3)	0.4518 (3)	0.1333 (3)	0.0660 (10)

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

Table 2. Bond distances (\AA), bond angles ($^\circ$) and selected torsion angles ($^\circ$) with e.s.d.'s in parentheses

C(1)–C(2)	1.376 (4)	C(10)–C(11)	1.367 (6)
C(2)–C(3)	1.376 (6)	C(11)–C(12)	1.365 (5)
C(3)–C(4)	1.376 (6)	C(12)–C(13)	1.375 (5)
C(4)–C(5)	1.381 (5)	C(13)–C(8)	1.382 (4)
C(5)–C(6)	1.375 (4)	C(7)–C(14)	1.315 (3)
C(6)–C(1)	1.386 (4)	C(14)–N	1.225 (3)
C(6)–C(7)	1.500 (3)	N–C(15)	1.430 (3)
C(7)–C(8)	1.473 (4)	C(15)–C(16)	1.382 (4)
C(8)–C(9)	1.393 (4)	C(15)–C(17)	1.360 (4)
C(9)–C(10)	1.362 (5)	C(16)–C(17)	1.384 (4)
C(1)–C(2)–C(3)	119.9 (3)	C(8)–C(9)–C(10)	121.2 (3)
C(2)–C(3)–C(4)	120.1 (4)	C(9)–C(10)–C(11)	119.9 (3)
C(3)–C(4)–C(5)	119.9 (4)	C(10)–C(11)–C(12)	120.2 (4)
C(4)–C(5)–C(6)	120.4 (3)	C(11)–C(12)–C(13)	120.2 (3)
C(5)–C(6)–C(1)	119.3 (2)	C(12)–C(13)–C(8)	120.6 (3)
C(6)–C(1)–C(2)	120.3 (3)	C(13)–C(8)–C(9)	117.8 (3)
C(1)–C(6)–C(7)	120.3 (2)	C(7)–C(14)–N	171.5 (3)
C(5)–C(6)–C(7)	120.3 (2)	C(14)–N–C(15)	125.7 (2)
C(6)–C(7)–C(8)	123.1 (2)	N–C(15)–C(16)	122.6 (2)
C(6)–C(7)–C(14)	117.2 (2)	N–C(15)–C(17)	117.2 (2)
C(7)–C(8)–C(9)	120.4 (2)	C(16)–C(15)–C(17)	120.1 (2)
C(7)–C(8)–C(13)	121.8 (2)	C(15)–C(16)–C(17)	119.0 (2)
C(8)–C(7)–C(14)	119.7 (2)	C(15)–C(17)–C(16)	120.9 (3)
C(1)–C(6)–C(7)–C(8)	47.2 (3)	C(13)–C(8)–C(7)–C(6)	19.6 (3)
C(5)–C(6)–C(7)–C(14)	44.9 (3)	C(14)–N–C(15)–C(16)	-5.5 (4)
C(9)–C(8)–C(7)–C(14)	18.2 (3)	C(14)–N–C(15)–C(17)	176.0 (3)

Symmetry code: (i) $1-x, 1-y, -z$.

N–C and the two C–C=C angles average to 124 (3), 121 (5) and 119 (4) $^\circ$ respectively. Of particular interest is the conformation of the *N*-phenyl ring with respect to the ketenimine fragment.

As in several *N*-phenyl substituted ketenimines (Runge, 1980; Naqvi & Wheatley, 1970) the angle between the phenyl ring and the C=N–C plane is small [4.6 (3) $^\circ$] which suggests that conjugation of the *N*-phenyl π system with the C=N bond is energetically preferred to conjugation with the lone electron pair of nitrogen. In the presence of one methyl group *ortho* to N at the greater distance from the ketenimine fragment

the planarity of the system is preserved, but in the case of two methyl groups *ortho* to N the phenyl ring is severely twisted [dihedral angle 63 (1) $^\circ$] because of non-bonding interactions with the C=C=N chain (Jochims *et al.*, 1984). However, deviations from coplanarity of the *N*-phenyl ring and the C=N–C plane have also been reported for ketenimines in which the *N*-phenyl ring had *p*-bromo and *p*-nitro substituents (Lambrech *et al.*, 1981); the observed deviation from planarity for the *p*-nitro compound amounts to 15 $^\circ$ and for the three independent molecules of the *p*-bromo compound the deviations are 5, -15 and 30 $^\circ$ respectively. These rather large twists exemplify the small difference in energy between the conjugation of C=N/*N*-phenyl ring and nitrogen lone pair/*N*-phenyl ring. *Ab initio* SCF calculations (Jochims *et al.*, 1984) on the model compound *N*-phenyl ketenimine support this view. For the linear arrangement the energy minimum was calculated for a configuration in which the *N*-phenyl ring was twisted 25 $^\circ$ with respect to the C=N–C plane, but the energy of the coplanar arrangement was only 0.9 kJ mol $^{-1}$ higher, which is illustrative of the low rotational barrier around the *N*-phenyl bond.

According to X-ray results on ketenimines (Runge, 1980; Jochims *et al.*, 1984) the C=C=N angle deviates

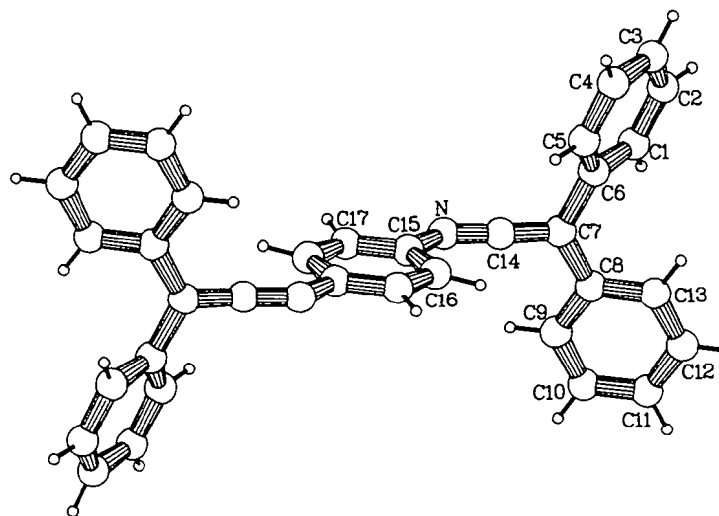


Fig. 1. Perspective view of the molecule with atom numbering.

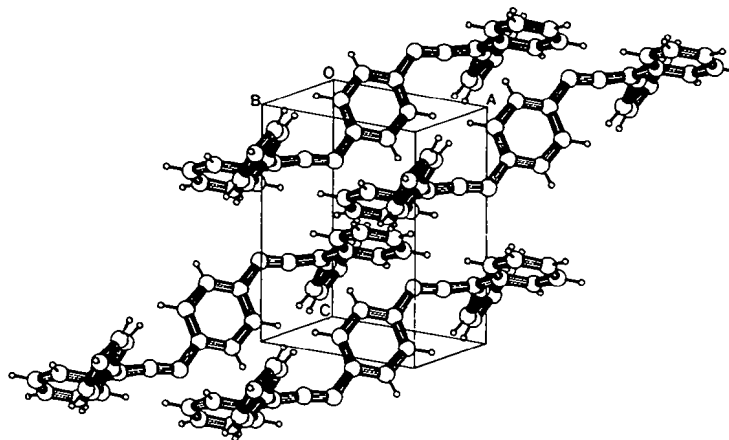


Fig. 2. Arrangement of the molecules in the unit cell.

significantly from linearity. This angle is $171.5(3)^\circ$ in the title compound and its value compares very well with the average of $172(1)^\circ$ with a range of 170.2 – 176.2° for the ten structures contained in the Cambridge Crystallographic Database. The deviation is in-plane with the central part of the molecule. In the literature this deviation of linearity has been ascribed to packing effects (Bullough & Wheatley, 1957; Naqvi & Wheatley, 1970; Lambrecht *et al.*, 1981). However, the fact that this non-linearity was observed in all reported ketenimine structures that all have different crystallographic environments warrants the view that it is an intrinsic property of the ketenimine moiety. This view is supported by results of SCF calculations mentioned above in which optimization of the $C=C=N$ angle led to an energy minimum with an angle of 175° and a twist angle of the *N*-phenyl ring of 25° . This minimum is 1.8 kJ mol^{-1} lower than the minimum obtained with the model in which this angle was constrained to 180° . From the X-ray observations and the results of the SCF calculations it may be concluded that the packing effects mainly affect the orientation of the *N*-phenyl ring with respect to the ketenimine π system, rather than the linearity of the $C=C=N$ chain.

The stacking of the molecules in the unit cell is shown in Fig. 2. The twists of the terminal phenyl rings, mentioned before, are necessary to prevent severe non-bonded repulsions between the aromatic rings.

Nevertheless, some intramolecular contacts are short: $H(C9)\cdots C14$, $H(C13)\cdots C6$, $H(C13)\cdots C1$ and $H(C5)\cdots C14$ which are $2.55(1)$, $2.71(1)$, $2.73(1)$ and $2.74(1) \text{ \AA}$ respectively.

References

- BULLOUGH, R. K. & WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 233–237.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 JOCHIMS, J. C., LAMBRECHT, J., BURKERT, U., ZSOLNAL, L. & HUTTNER, G. (1984). *Tetrahedron*, **40**, 893–903.
 LAMBRECHT, J., GAMBKE, B., VON SEYERL, J., HUTTNER, G., KOLLMANNBERGER-VON NELL, G., HERZBERGER, S. & JOCHIMS, J. C. (1981). *Chem. Ber.* **114**, 3751–3771.
 NAQVI, R. R. & WHEATLEY, P. J. (1970). *J. Chem. Soc. A*, pp. 2053–2058.
 RUNGE, W. (1980). *The Chemistry of Ketenes, Allenes and Related Compounds*, edited by S. PATAL, pp. 45–98. New York: John Wiley.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.
 SIKKEMA, D. J., MOLENAAR, E. & VAN GULDENER, D. B. (1976). *Recl Trav. Chim. Pays-Bas*, **95**, 154–156.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1989). **C45**, 485–489

Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. XI. 5,6,7,8-Tetrahydro-*N,N'*-ditosyl-4*H*-dibenzo[*b,i*][1,5,7]oxadiazecine. XII. 4,5,6,7,8,9,10,11-Octahydro-*N,N'*-ditosyl-1-oxa-5,10-diazadibenzo[*b,l*]cyclotridecene

BY A. STĘPIEŃ AND M. J. GRABOWSKI

Department of Crystallography, Institute of Chemistry, University of Łódź, Nowotki 18, 91-416 Łódź, Poland

R. GLINKA

Institute of Chemistry and Technology of Drugs, School of Medicine, Narutowicza 120a, 90-145 Łódź, Poland

AND P. SABATINO* AND L. RIVA DI SANSEVERINO

Dipartimento di Scienze Mineralogiche, Università di Bologna, Piazza Porta S. Donato 1, 40126 Bologna, Italy

(Received 13 July 1988; accepted 14 October 1988)

Abstract. (XI) $C_{29}H_{28}N_2O_5S_2$, $M_r = 548.68$, monoclinic, $P2_1/c$, $a = 13.917(4)$, $b = 9.970(4)$, $c = 19.711(6) \text{ \AA}$, $\beta = 101.15(2)^\circ$, $V = 2683.33 \text{ \AA}^3$, $Z =$

4, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.24 \text{ mm}^{-1}$, $D_x = 1.358 \text{ g cm}^{-3}$, $F(000) = 1152$. Diffractometer data at room temperature, $R = 0.0368$ for 2735 reflections with $I > 2.5\sigma(I)$. The heterocycle is in a boat-like conformation. The tosyl groups adopt an *exo, exo* conformation. The heterocycle system and the tosyl

* Present address: Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy.