$\varphi_{OO} = 173{\cdot}9\ (10)°$ and $\varphi_{OC} = -68{\cdot}1\ (13)°$ for molecule *A* and $\varphi_{OO} = -176{\cdot}3\ (11)°$ and $\varphi_{OC} = -57{\cdot}0\ (17)°$ for molecule *B*.

In molecule *A* the dioxolane ring pucker is C(9)-*endo*–O(3′)*exo* with $P_\lambda = -78{\cdot}15°$ and $\lambda_{m,\max} = 31{\cdot}46°$. C(9) and O(3′) deviate with respect to the three-atom plane by −0·31 (1) and 0·16 (1) Å respectively. In molecule *B* the ring assumes O(2′)*endo*–C(9)*exo* conformation with $P_\lambda = 71{\cdot}3°$, $\lambda_{m,\max} = 29{\cdot}9°$ and O(2′) and C(9) displaced by −0·22 (1) and 0·21 (2) Å respectively.

We have earlier reported the structure of the orthorhombic form of the title compound which was grown from Me_2SO (Mande, Seshadri & Viswamitra, 1988). The conformation of the nucleoside moiety in this structure was *anti*, C(3′)-*exo* and *gauche–gauche*, significantly different from that observed here, namely *syn*, C(1′)-*endo* and *trans–gauche*.

The two crystallographically independent molecules in the asymmetric unit exhibit base pairing with hydrogen bonds, N(7)*A*···H(1)–N(1)*B* (2·85 Å and 170·87°) and O(6)*A*···H(12)–N(2)*B* (2·97 Å and 150·34°). A similar hydrogen-bonding scheme has been observed in the crystal structure of 9-ethylguanine (Destro, Kistenmacher & Marsh, 1974). The crystal structure is also stabilized by base stacking and three other hydrogen bonds. Screw-related *A* molecules show partial base stacking as shown in Fig. 2 with C(6) and O(6) at a distance of 3·5 Å from the guanine ring plane. Molecule *B* does not show any base stacking. The bases form sheets parallel to the *ac* plane. Other hydrogen bonds contributing to the stability of the structure are N(2)*A*–H(12)*A*···O(6)*B* (2·95 Å, 143·83°), N(1)*A*–H(1)*A*···N(7)*B* (2·83 Å, 164·79°) and O*W*–H(2)*W*···O(3′)*A* (2·90 Å, 154·81°).

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Structure of 2,5a,9-Trimethyl-5a,6-dihydrotriphenodioxazine

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Abstract. $C_{21}H_{18}N_2O_2$, $M_r = 330{\cdot}39$, monoclinic, $P2_1/c$, $a = 6{\cdot}690\ (1)$, $b = 13{\cdot}611\ (2)$, $c = 19{\cdot}571\ (4)$ Å, $\beta = 113{\cdot}53\ (2)°$, $V = 1634\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}34$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 66{\cdot}0$ mm^{-1}, $F(000) = 696$, room temperature, final $R = 0{\cdot}066$ for 1059 independent reflections and 226 parameters. In spite of the presence of an atomic group in the molecule which exerts a perturbing action, most atoms are in a *quasi*planar disposition, which allows extended π-electron-charge delocalization.

Introduction. In the biosynthesis of ommochromes the reactivity of *o*-aminophenols plays a role of particular importance. Ommochromes are natural pigments widespread through all classes of insects, crustaceans and cephalopods (Butenandt & Schäfer, 1962). Their high photoreactivity under visible light puts these pigments in a crucial position on the scale of photoinduced excitation response. Present knowledge about the role of auxiliary pigments in the primary processes of vision suggests that ommochromes could act as screening or

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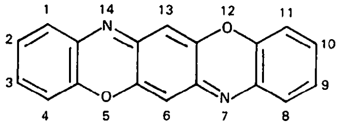
Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10$) *of the non*-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}
C(1)	9122 (11)	−1019 (5)	1761 (4)	44 (2)
C(2)	8951 (10)	−1956 (5)	2007 (3)	40 (2)
C(3)	6884 (11)	−2337 (5)	1851 (4)	42 (2)
C(4)	5028 (10)	−1773 (5)	1480 (3)	41 (2)
O(5)	3352 (6)	−319 (3)	882 (2)	35 (1)
C(6)	1594 (9)	1110 (4)	271 (3)	33 (2)
N(7)	24 (8)	2687 (3)	−223 (3)	36 (1)
C(8)	−1567 (10)	4191 (5)	−862 (3)	40 (2)
C(9)	−1411 (10)	5076 (5)	−1192 (3)	38 (2)
C(10)	601 (11)	5370 (5)	−1161 (4)	51 (2)
C(11)	2407 (11)	4801 (5)	−815 (4)	48 (2)
O(12)	4090 (6)	3365 (3)	−167 (2)	40 (1)
C(13)	5710 (10)	1911 (5)	442 (3)	39 (2)
N(14)	7445 (7)	461 (4)	1070 (3)	35 (1)
C(15)	7253 (9)	−440 (4)	1387 (3)	34 (2)
C(16)	5218 (10)	−843 (5)	1276 (3)	36 (3)
C(17)	5686 (9)	996 (5)	803 (3)	31 (2)
C(18)	3623 (9)	736 (4)	910 (3)	30 (2)
C(19)	3906 (10)	2466 (4)	118 (3)	32 (2)
C(20)	1765 (9)	2151 (4)	54 (3)	32 (2)
C(21)	2249 (10)	3917 (5)	−505 (3)	38 (2)
C(22)	249 (10)	3618 (4)	−520 (3)	36 (2)
C(23)	10973 (12)	−2564 (5)	2427 (4)	54 (2)
C(24)	3765 (11)	1126 (5)	1662 (4)	42 (2)
C(25)	−3410 (12)	5729 (5)	−1572 (4)	55 (2)

tuning antennas. Oxidative condensation of *o*-aminophenols is well known to be the prominent process in the formation of these pigments. In our laboratory, the oxidation of *o*-aminophenols by ferricyanide, in acid medium, has yielded phenoxazines, phenoxazinones, triphenodioxazines and dihydrotriphenodioxazines (Bolognese, Piscitelli & Scherillo, 1983; Bolognese, Liberatore & Scherillo, 1988). The lack of structural characterizations of molecules of the triphenodioxazine system (I) prompted us to try to crystallize those synthesized molecules having a skeleton related to (I), in forms suitable for structure determination by X-ray diffraction. The title compound is the first example.



(I)

Experimental. The synthesis of the title compound has been described by Bolognese *et al.* (1988). Very thin, needle-shaped crystals, elongated along [10$\bar{1}$], were grown from CCl_4. The rather poor quality of the crystals was indicated by the large value of the spread on ω of reflection intensities. A crystal of dimensions $0{\cdot}50 \times 0{\cdot}08 \times 0{\cdot}08$ mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer, Ni-filtered Cu $K\alpha$ radiation. Cell dimensions were determined by a least-squares procedure applied to the setting angles of 20 reflections in the θ range $10 \leq \theta \leq 25°$. Out of the total 3268 independent reflections measured by the ω/θ scan technique with $\theta \leq 73°$, $0 \leq h \leq 8$, $0 \leq k \leq 17$, $-24 \leq l \leq 24$, 1059 having $I_o > 2\sigma(I_o)$ were taken as observed. Three monitoring reflections showed no significant intensity variations throughout data collection. Lp correction absorption ignored. The structure was solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares minimized $\sum w(\Delta F)^2$, $w = 1/\sigma^2(F)$. The H atoms, located in part from ΔF synthesis and in part placed at their calculated stereochemical positions, were included in the structure-factor calculations with isotropic thermal factors derived from those of the carrier atoms, but not refined. 226 refined parameters included overall scale factor, positional and anisotropic thermal parameters of the non-H atoms. Final $R = 0{\cdot}066$, $wR = 0{\cdot}075$, $S = 1{\cdot}51$. Final $\Delta/\sigma_{max} = 0{\cdot}01$; final difference electron density within $\pm 0{\cdot}25$ e $Å^{-3}$.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed by the Enraf–Nonius (1979) system of programs (*SDP*) on a PDP 11/34 computer of the Centro di Metodologie Chimico-fisiche dell'Univeristà di Napoli. Final atomic parameters of the non-H atoms are listed in Table 1.*

Discussion. A view of the molecule with the atom-labelling scheme is shown in Fig. 1. The crystal packing, presented in Fig. 2, shows pairs of molecules related by a centre of symmetry placed side by side to form infinite corrugated ribbons running along **a**. Neither particular intermolecular interactions nor contacts shorter than the sum of the atomic van der Waals radii are detectable. Thus, the molecular geometry can be considered as scarcely affected by the crystal forces.

Apart from C(18) and C(24) of sp^3 character, all the other non-H atoms form a roughly planar arrangement [maximum displacement 0·157 (7) Å], achieving the necessary condition for a π-electron charge delocalized throughout the molecule. Of the five fused six-membered rings, *A*, *D* and *E* (Fig. 1) are approximately planar. The values of the χ^2 distribution for their mean planes, respectively 70, 75 and 9, indicate a distance-dependent influence of the perturbing group C(6)—C(18)—C(24). Ring *C* displays an almost perfect half-chair conformation with C(18) and C(6) on the opposite sides of the ring mean plane, in such a way as to relax the contact between the methyl C(24) atom and H(2C6), which is linked to C(6) in equatorial position.

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* 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 51305 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Ring *B* has a distorted conformation intermediate between a half chair and a sofa, in which O(5) and C(18) are the atoms with the largest out-of-plane amplitudes. The values of the ring-puckering parameters according to Cremer & Pople (1975) are: $Q = 0{\cdot}375\ (9)$ Å, $\theta = 125\ (1)°$, $\varphi = 150\ (4)°$ for ring *C* and $Q = 0{\cdot}383\ (9)$ Å, $\theta = 114\ (1)°$, $\varphi = 341\ (4)°$ for ring *B*.

Scrutiny of the bond lengths in Table 2 confirms the presence of an extended π-electron delocalization. In fact, if we focus our attention on the inner *B–C–D* three-ring system we can observe that, whilst the bonds to C(6) and C(18) are typical single bonds and the bonds N(14)—C(17), N(7)—C(20) and C(13)—C(19) are slightly longer than a typical double bond, all the other distances exhibit varying extents of double-bond character. In particular, if the well known relationships between bond lengths and bond orders are used (Liquori & Vaciago, 1956; Burke-Laing & Laing, 1976; Giordano, 1988), bond orders ranging from 1·2 to 1·3 are found for the bonds C(15)—N(14), C(13)—C(17), O(12)—C(19), O(12)—C(21) and C(16)—O(5). Thus, an unbroken line of π-electron charge connects the two benzenoid rings *A* and *E*. The bond-order value of N(7)—C(22) is smaller than 1·1 and makes the classification of this bond uncertain.

The present structure can give an appropriate model of the triphenodioxazine system (I), by removal of the segment O(5)···N(7) and imposition of a molecular-symmetry centre.

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

The ranges of the e.s.d.'s are 0·006–0·008 Å (mean 0·0074 Å) for the bond lengths and 0·5–0·7° (mean 0·6°) for the valence angles.

C(1)—C(2)	1·384	C(9)—C(25)	1·528
C(1)—C(15)	1·410	C(10)—C(11)	1·366
C(2)—C(3)	1·392	C(11)—C(21)	1·370
C(2)—C(23)	1·518	O(12)—C(19)	1·370
C(3)—C(4)	1·392	O(12)—C(21)	1·367
C(4)—C(16)	1·348	C(13)—C(17)	1·435
O(5)—C(16)	1·376	C(13)—C(19)	1·349
O(5)—C(18)	1·446	N(14)—C(15)	1·402
C(6)—C(18)	1·520	N(14)—C(17)	1·303
C(6)—C(20)	1·496	C(15)—C(16)	1·403
N(7)—C(20)	1·296	C(17)—C(18)	1·518
N(7)—C(22)	1·427	C(18)—C(24)	1·532
C(8)—C(9)	1·390	C(19)—C(20)	1·452
C(8)—C(22)	1·372	C(21)—C(22)	1·388
C(9)—C(10)	1·382		

C(2)—C(1)—C(15)	121·1	C(19)—C(13)—C(17)	122·2
C(1)—C(2)—C(3)	118·7	C(13)—C(17)—C(18)	117·4
C(2)—C(3)—C(4)	120·6	C(17)—C(18)—C(6)	111·8
C(3)—C(4)—C(16)	120·2	C(20)—N(7)—C(22)	116·6
C(4)—C(16)—C(15)	121·5	N(7)—C(22)—C(21)	120·6
C(1)—C(15)—C(16)	117·8	C(22)—C(21)—O(12)	121·6
C(16)—O(5)—C(18)	115·0	C(21)—O(12)—C(19)	118·5
O(5)—C(18)—C(17)	109·5	O(12)—C(19)—C(20)	118·4
C(18)—C(17)—N(14)	122·6	C(19)—C(20)—N(7)	124·1
C(17)—N(14)—C(15)	116·1	C(22)—C(8)—C(9)	120·3
N(14)—C(15)—C(16)	121·9	C(8)—C(9)—C(10)	118·8
C(15)—C(16)—O(5)	119·4	C(9)—C(10)—C(11)	120·7
C(18)—C(6)—C(20)	114·0	C(10)—C(11)—C(21)	120·5
C(6)—C(20)—C(19)	116·1	C(11)—C(21)—C(22)	119·5
C(20)—C(19)—C(13)	122·8	C(21)—C(22)—C(8)	120·1

Finally, it is worth noting that the difference between the values of the endocyclic bond angles at the two O atoms [C(16)—O(5)—C(18) 115·0 (5)° and C(19)—O(12)—C(21) 118·5 (5)°] is significant and can be easily accounted for. In fact, the variation of these angles complies with the sum of the bond orders adjacent to the O atoms, since the values of these bond orders are all 1·3 except that for the O(5)—C(18) bond which is 1·0.

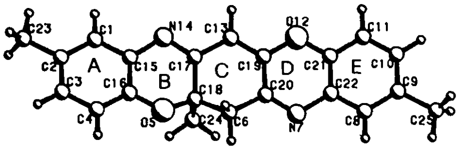

Fig. 1. View of the molecule showing the atom-labelling scheme.

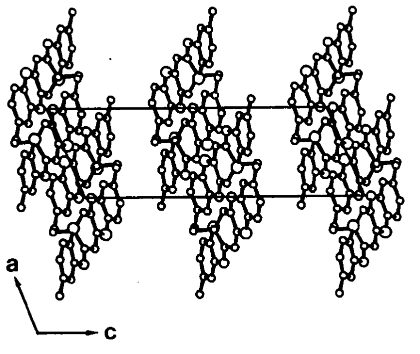

Fig. 2. Projection of the crystal structure down **b**. For the sake of clarity the H atoms are omitted.

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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. X. *N,N'*-Ditosyl-6,7,8,13-tetrahydrodibenz[*b,g*][1,4,6]oxadiazonine

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Abstract. $C_{28}H_{26}N_2O_5S_2$, $M_r = 534{\cdot}6$, monoclinic, $P2_1/c$, $a = 13{\cdot}734\,(6)$, $b = 30{\cdot}818\,(9)$, $c = 13{\cdot}303\,(7)$ Å, $\beta = 110{\cdot}87\,(3)°$, $V = 5261\,(4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}350\,(1)$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 20{\cdot}61$ cm^{-1}, $F(000) = 2240$, room temperature, $R = 0{\cdot}0587$ for 4018 reflections with $I > 3\sigma(I)$. There are two different molecules in the asymmetric unit: molecule 1 is in an *exo,exo* modification and molecule 2 in an *exo,endo* modification. The nine-membered ring is in a quasi-chair conformation for both molecules.

Introduction. This paper is a continuation of the study of the structure–biological-activity relationship of dibenzoxadiazacycloalkanes. The title compound was obtained by reaction of the sodium salt of *N*-{2-[2-(*p*-toluenesulfonamide)methoxy]phenyl}toluenesulfonamide with methylene dibromide. The formula was confirmed by mass spectrometry and IR and NMR spectra (Glinka, 1985). The compound shows weak neuroleptic activity (Glinka, 1986).

Experimental. Light-yellow crystals from ethanol, room temperature; crystal dimensions 0·1 × 0·2 × 0·4 mm. CAD-4 diffractometer using θ–2θ scan technique; unit-cell parameters from 25 reflections in the θ range 9·0–46·3°; graphite-monochromatized Cu $K\alpha$ radiation; range of h, k, and l: 0 to 15, 0 to 37 and −15 to 15, respectively. 7199 independent reflections measured to $(\sin\theta)/\lambda = 0{\cdot}63$ Å^{-1}, data not corrected for absorption, $R_{\mathrm{int}} = 0{\cdot}0477$; standard reflection 372, maximum change 2·2%. 4018 reflections with $I > 3\sigma(I)$ used in calculations. Solution by direct methods using *SHELX*76 (Sheldrick, 1976); all H atoms located from a difference map; refinement by a full-matrix least-squares procedure on F magnitudes (875 parameters); each symmetry-independent molecule was refined in a separate block. Because of high thermal vibrations (or disorder) of atoms of the benzene rings of both tosyl groups, in last two refinement cycles constraints were applied to the geometry of these rings. Refinement to final $R = 0{\cdot}0587$, $S = 2{\cdot}26$, unit weights; largest peak on final difference map 0·36 e Å^{-3}; ratio of max. shift/e.s.d. = 0·74; scattering factors from *SHELX*76.

Discussion. The final atomic coordinates are listed in Table 1,* bond lengths and angles in Table 2. A view of the molecular structure with the atomic numbering scheme is shown in Fig. 1. The geometry of the molecule was calculated using the *ORFFE*3 program (Busing, Martin & Levy, 1971).

There are two different molecules in the asymmetric unit. The difference is mainly in the orientation of the tosyl groups: in molecule 1 they are oriented away from the heterocyclic ring while in molecule 2 the orientation

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51166 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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