$\omega/2\theta$ scans
Absorption correction: none
4848 measured reflections
2025 independent reflections
1392 reflections with $I > 2\sigma(I)$
$h = 0 \rightarrow 7$
$k = -21 \rightarrow 21$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1.4%

Refinement

Refinement on F^2
$R(F) = 0.036$
$wR(F^2) = 0.074$
$S = 1.042$
2026 reflections
161 parameters
H-atom positional parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.225$ e Å^{-3}
$\Delta\rho_{\min} = -0.248$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.017 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cl—O11	1.417 (2)	C2—N1	1.339 (2)
Cl—O13	1.425 (2)	C2—N2	1.366 (3)
Cl—O14	1.425 (2)	C2—C3	1.397 (3)
Cl—O12	1.432 (2)	C3—C4	1.363 (3)
O1—C1	1.228 (2)	C4—C5	1.387 (3)
C1—N3	1.326 (3)	C5—C6	1.359 (3)
C1—N2	1.386 (2)	C6—N1	1.351 (3)
O11—Cl—O13	109.43 (11)	O1—C1—N2	120.7 (2)
O11—Cl—O14	110.22 (12)	N3—C1—N2	115.3 (2)
O13—Cl—O14	109.76 (13)	N1—C2—N2	120.2 (2)
O11—Cl—O12	109.63 (11)	N2—C2—C3	121.4 (2)
O13—Cl—O12	109.51 (11)	C4—C3—C2	119.1 (2)
O14—Cl—O12	108.28 (11)	C2—N1—C6	122.9 (2)
O1—C1—N3	124.0 (2)	C2—N2—C1	125.9 (2)

Table 2. *Hydrogen-bond parameters (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	*A*···H···*A*
N1—HN1···O1	0.85 (2)	1.92 (2)	2.606 (2)	137 (2)	
N1—HN1···O13^{i}	0.87 (3)	2.47 (2)	3.105 (3)	132 (2)	90 (1)
N2—HN2···O14	0.79 (2)	2.17 (2)	2.950 (2)	170 (2)	
N3—HN31···O1^{ii}	0.83 (2)	2.15 (3)	2.950 (3)	164 (2)	
N3—HN32···O12	0.81 (2)	2.21 (3)	3.002 (3)	168 (3)	

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $-x, -y, 1 - z$.

All H atoms have been localized from difference Fourier maps and refined with fixed isotropic thermal displacement parameters.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Data reduction: *SDP/PDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

This work has been supported by the Bulgarian National Science Foundation, Project ch-588.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1081). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 973–979

Isomerism/Tautomerism in Hydrazones Derived from Thiophenaldehydes and 2-Hydrazinoquinoline

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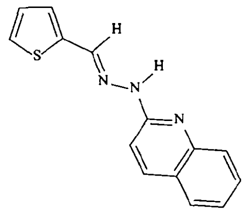
(*Received 6 November 1996; accepted 24 January 1997*)

Abstract

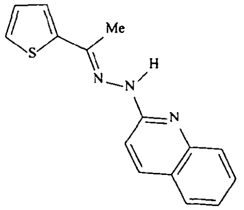
The structures of 2-thiophenecarbaldehyde 2-quinolylhydrazone, $C_{14}H_{11}N_3S$, (1), 2-acetylthiophene 2-quinolylhydrazone, $C_{15}H_{13}N_3S$, (2), 2(1*H*)-quinolone 5-bromo-2-thienylmethylidenehydrazone, $C_{14}H_{10}BrN_3S$, (3), and 5-chloro-2-thiophenecarbaldehyde 2-quinolylhydrazone, $C_{14}H_{10}ClN_3S$, (4), show that (1), (2) and (4) exist as the *anti–E* isomer, while (3) is the tautomer of the *syn–Z* isomer, being protonated on the quinoline nitrogen rather than on the exocyclic nitrogen. The photochemical isomerization/tautomerization of (3) to the *anti–E* isomer is discussed.

Comment

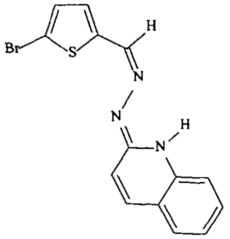
Hydrazones have been widely studied as chelating ligands for the spectrophotometric and fluorimetric determination of trace metal ions (Geldard & Lyons, 1964; Katyal & Dutt, 1975; Singh, Jain & Singh, 1972; Galiano-Roth & Collum, 1988; Desgupta, Zhang, Schulze & Marx, 1994). Less studied are those derived from thiophenaldehydes and quinolylhydrazines of which (1) is the parent. These can exist as either *anti-E* or *syn-Z* isomers with the former having the potential to function as a tridentate ligand while the latter should be bidentate. While various examples of these hydrazones have been used as analytical reagents, relatively little attention appears to have been paid to determining the specific isomer(s) involved in complex formation and in the few studies reported to address this point, there are conflicts with previous structural assignments (Berge, 1983; Martinez de la Barrera, Laserna & Garcia-Sanchez, 1983*a*,*b*; Gimenez-Plaza & Bosch-Ojeda, 1983*a*,*b*; Garcia-Sanchez & Hernandez-Lopez, 1985; Hernandez-Lopez & Garcia-Sanchez, 1985; Karabatsos, Shapiro, Vane, Fleming & Ratka, 1963; Going, 1968; Bell & Rose, 1968, 1969). In order to more efficiently develop applications of quinolylhydrazones of thiophenaldehyde as metal-specific ligands, we set out to establish specific spectroscopic characteristics which could be used to unequivocally distinguish between the *E* and *Z* isomers. As part of this study we have determined the structures of 2-thiophenecarbaldehyde 2-quinolylhydrazone, (1), 2-acetylthiophene 2-quinolylhydrazone, (2), 2(1*H*)-quinolone 5-bromo-2-thienylmethylidenehydrazone, (3), and 5-chloro-2-thiophenecarbaldehyde 2-quinolylhydrazone, (4).



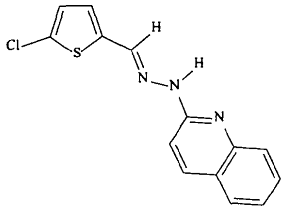
(1)



(2)



(3)



(4)

All compounds participate in N—H···N hydrogen bonding in the solid. For (2) and (3), this involves the pairwise interactions N2—H2*n*···N3$^{\rm i}$ and N2$^{\rm i}$—H2*n*$^{\rm i}$···N3 in (2) [H2*n*···N3$^{\rm i}$ 2.34 (4) Å and N2—H2*n*···N3$^{\rm i}$ 173 (3)°; symmetry code: (i) $1-y$, $1-x$, $\frac{3}{2}-z$] and N3—H3*n*···N1$^{\rm ii}$ and N1···H3*n*$^{\rm ii}$—N3$^{\rm ii}$ in (3) [H3*n*···N1$^{\rm ii}$ 2.25 (5) Å and N3—H3*n*···N1$^{\rm ii}$ 160 (5)°; symmetry code: (ii) y, x, $-z$]. These are shown in Figs. 5 and 6, respectively. In (1), the interaction

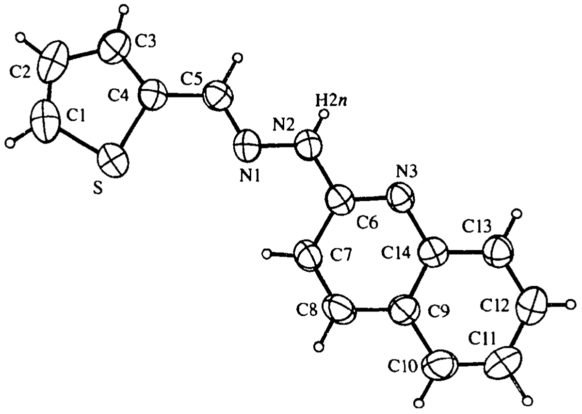


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

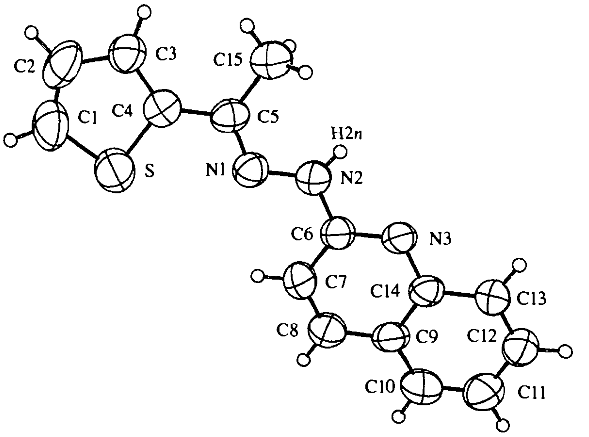


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (2). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

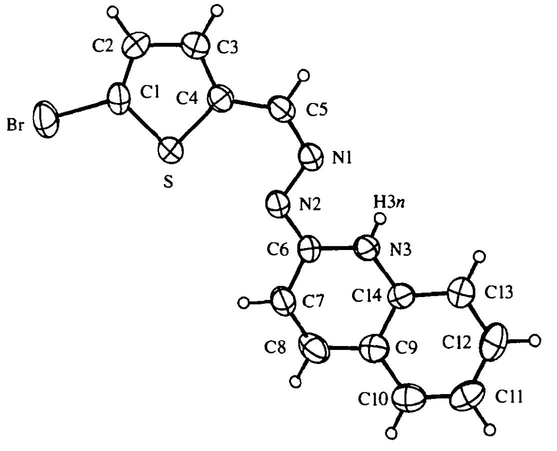


Fig. 3. *ORTEP*II (Johnson, 1976) drawing of (3). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

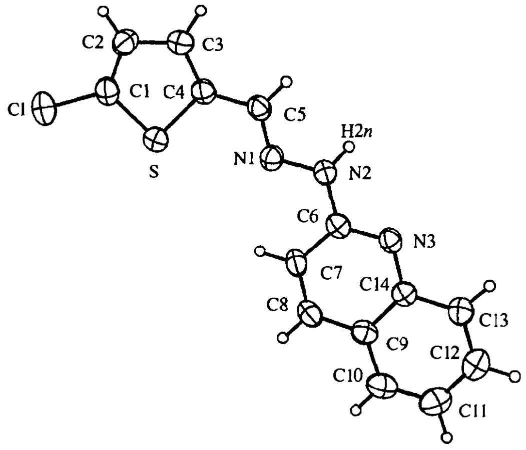


Fig. 4. *ORTEP*II (Johnson, 1976) drawing of (4). Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are drawn arbitrarily small.

involves N2—H2*n*···N3^{iii} [H2*n*···N3^{iii} 2.34 (3) Å and N2—H2*n*···N3^{iii} 160 (2)°; symmetry code: (iii) $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$], with N3 then being hydrogen bonded to H2*n* of another molecule at $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$. This motif continues parallel to **b** as shown in Fig. 7. An analogous situation is seen in (4) [H2*n*···N3^{iv} 2.27 (3) Å and N2—H2*n*···N3^{iv} 168 (3)°; symmetry code: (iv) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$] with the motif continuing parallel to **a**. All four molecules are substantially planar as evidenced by the torsion angles along the N3—C6—N2—N1—C5—C4—C3 backbone which differ by no more than 6° from 0 or ±180°. The results clearly show that while (1), (2) and (4) exist as the 'fully extended' *anti–E* isomers, (3) is the *syn–Z* isomer of the tautomer which is protonated at N3 rather than at N2. This feature is evidenced not only by the location and refinement of an H atom (H3*n*) attached to N3 but also by the N1—N2 and N2—C6 distances which are significantly longer and shorter, respectively, than the corresponding distances in (1), (2) and (4), as well as by the N3—C6 distance which is also significantly longer than its counterparts in the other three compounds. Additionally, the C4—C5—N1 angle in (3) is much larger than in (1), (2) and (4). All other distances and angles are comparable with those found in related species (Battaglia, Corradi, Pelosi & Tarasconi, 1989; Leloux, Kyriakidis, Keramidis, Christidis & Rentzeperis, 1993; Amari, Pelizzi, Pelizzi, Predieri & Sartori, 1994; de la Concepcion Foces-Foces, Cano, Claramunt, Fruchier & Elguero, 1988; Mathew & Palenik, 1971).

The finding that (3) adopts the *syn–Z* configuration is surprising considering that N2 is no longer protonated and cannot be part of intramolecular hydrogen bonding with the heteroatom of the aldehyde residue, which has been proposed previously to explain the stability of the *syn–Z* configuration in similar systems (Asano, Okada & Herkstroeter, 1989; Lewis & Yoon, 1994; Arai, Moriyama & Tokumaru, 1994). Preliminary photolysis studies clearly indicate that the *anti–E* isomer is the thermodynamically stable one for (1), (2) and (4), and that (3) is readily and completely converted to the *anti–E* form. Thus, the observed isomer appears to be only metastable (Vang & Wacholtz, 1996). A

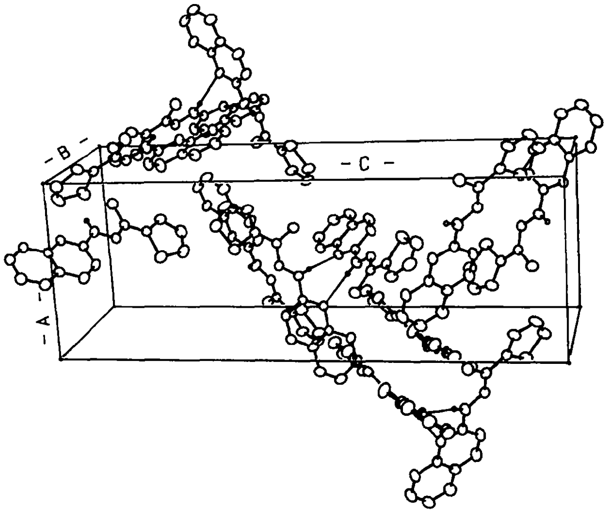


Fig. 5. Unit-cell contents for (2) showing the pairwise hydrogen-bonding interactions.

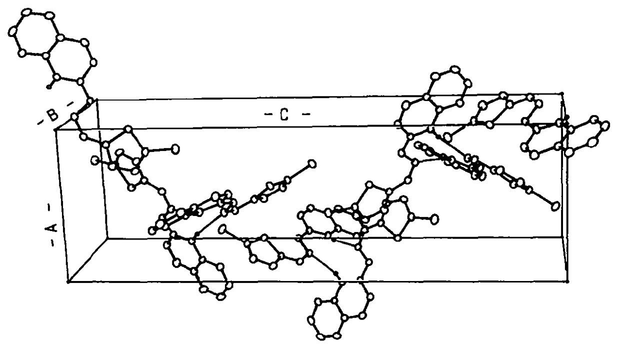


Fig. 6. Unit-cell contents for (3) showing the pairwise hydrogen-bonding interactions.

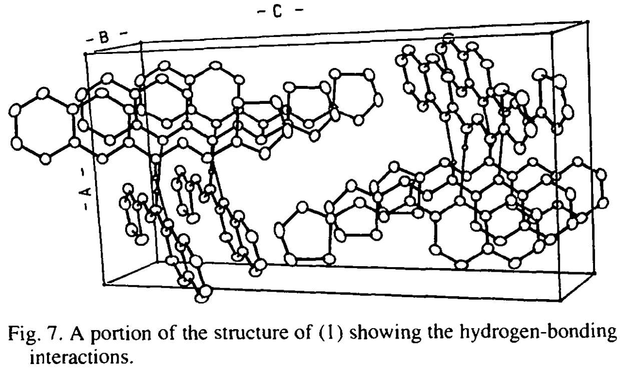


Fig. 7. A portion of the structure of (1) showing the hydrogen-bonding interactions.

possible explanation for the moderate stability of the *syn–Z* isomer for (3) is an augmentation of the formal delocalization of the electron density throughout the molecule, as supported by visible spectroscopic studies (Berge, 1994), due to the presence of the electron-rich bromine substituent.

Experimental

Compounds (1)–(4) were synthesized according to the method of Berge (1983) and crystals for the present study were obtained from ethanol [for compounds (1), (3) and (4)] or water/ethanol [for compound (2)] solutions. These were mounted on thin glass fibres with epoxy cement.

Compound (1)

Crystal data

$C_{14}H_{11}N_3S$
$M_r = 253.32$
Monoclinic
$P2_1/c$
$a = 11.188\,(1)$ Å
$b = 4.746\,(1)$ Å
$c = 23.012\,(2)$ Å
$\beta = 92.05\,(1)°$
$V = 1221.1\,(3)$ Å^3
$Z = 4$
$D_x = 1.38$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–16°$
$\mu = 0.25$ mm^{-1}
$T = 293$ K
Column
0.45 × 0.28 × 0.25 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2575 measured reflections
2156 independent reflections
1428 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 5$
$l = -27 \rightarrow 27$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.048$
$S = 1.45$
1428 reflections
207 parameters
All H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\rm max} = 0.009$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

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

	x	y	z	$U_{\rm eq}$
S1	0.19804 (6)	0.5593 (2)	0.40592 (3)	0.0637 (2)
N1	0.3287 (2)	0.1791 (4)	0.32683 (8)	0.0426 (5)
N2	0.3778 (2)	−0.0015 (4)	0.28851 (8)	0.0436 (5)
N3	0.3507 (1)	−0.3334 (4)	0.21666 (8)	0.0375 (5)
C1	0.2163 (3)	0.7879 (6)	0.4625 (1)	0.0653 (8)
C2	0.3310 (3)	0.8220 (6)	0.4785 (1)	0.0614 (8)
C3	0.4080 (2)	0.6613 (6)	0.4449 (1)	0.0516 (7)
C4	0.3494 (2)	0.5051 (5)	0.4035 (1)	0.0414 (6)
C5	0.3988 (2)	0.3141 (5)	0.3618 (1)	0.0436 (6)
C6	0.3018 (2)	−0.1438 (5)	0.25046 (9)	0.0376 (6)
C7	0.1781 (2)	−0.0805 (6)	0.2485 (1)	0.0481 (6)
C8	0.1065 (2)	−0.2060 (6)	0.2084 (1)	0.0509 (7)
C9	0.1533 (2)	−0.4077 (5)	0.1700 (1)	0.0428 (6)
C10	0.0832 (2)	−0.5454 (6)	0.1269 (1)	0.0553 (7)
C11	0.1333 (2)	−0.7416 (6)	0.0919 (1)	0.0587 (8)
C12	0.2543 (2)	−0.8059 (6)	0.0990 (1)	0.0549 (7)
C13	0.3247 (2)	−0.6730 (5)	0.1401 (1)	0.0464 (6)
C14	0.2766 (2)	−0.4671 (5)	0.17661 (9)	0.0383 (6)
H2*n*	0.452 (2)	0.002 (5)	0.2834 (8)	0.057 (7)

Table 2. *Selected geometric parameters (Å, °) for (1)*

N1—N2	1.360 (3)	N3—C6	1.321 (3)
N1—C5	1.275 (3)	N3—C14	1.373 (3)
N2—C6	1.376 (3)	C4—C5	1.445 (3)
N2—H2*n*	0.85 (3)	C6—C7	1.416 (3)
N2—N1—C5	118.1 (2)	N1—C5—C4	119.6 (2)
N1—N2—C6	117.8 (2)	N2—C6—N3	116.7 (2)
N1—N2—H2*n*	120 (2)	N2—C6—C7	119.9 (2)
C6—N2—H2*n*	121 (2)	N3—C6—C7	123.4 (2)
C6—N3—C14	117.2 (2)		

Compound (2)

Crystal data

$C_{15}H_{13}N_3S$
$M_r = 267.35$
Tetragonal
$P4_32_12$
$a = 9.8543\,(7)$ Å
$c = 28.457\,(4)$ Å
$V = 2763.3\,(1)$ Å^3
$Z = 8$
$D_x = 1.29$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 11–15°$
$\mu = 0.223$ mm^{-1}
$T = 293$ K
Plate
0.53 × 0.46 × 0.36 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\rm min} = 0.901$, $T_{\rm max} = 0.923$
2520 measured reflections
2170 independent reflections

1279 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 32$
2 standard reflections
frequency: 120 min
intensity decay: −2.7%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.043$
$S = 1.242$
1279 reflections
176 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\rm max} = 0.011$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)*

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

	x	y	z	U_{eq}
S	0.9457 (1)	0.0039 (1)	0.58096 (4)	0.0926 (3)
N1	1.0955 (3)	−0.1359 (3)	0.65611 (9)	0.0592 (8)
N2	1.1507 (3)	−0.2110 (3)	0.6916 (1)	0.0702 (8)
N3	1.1520 (3)	−0.3936 (3)	0.73991 (9)	0.0594 (8)
C1	0.9425 (4)	0.1423 (4)	0.5464 (2)	0.096 (1)
C2	1.0386 (4)	0.2321 (4)	0.5575 (1)	0.093 (1)
C3	1.1190 (4)	0.1903 (3)	0.5957 (1)	0.074 (1)
C4	1.0807 (3)	0.0647 (3)	0.6127 (1)	0.0581 (9)
C5	1.1412 (3)	−0.0147 (3)	0.6501 (1)	0.0582 (9)
C6	1.1049 (3)	−0.3398 (3)	0.7008 (1)	0.0555 (9)
C7	1.0128 (4)	−0.4063 (3)	0.6708 (1)	0.073 (1)
C8	0.9761 (4)	−0.5333 (3)	0.6815 (1)	0.086 (1)
C9	1.0278 (3)	−0.5989 (3)	0.7217 (1)	0.061 (1)
C10	0.9942 (4)	−0.7318 (4)	0.7349 (1)	0.086 (1)
C11	1.0452 (4)	−0.7889 (4)	0.7747 (1)	0.083 (1)
C12	1.1305 (4)	−0.7137 (4)	0.8035 (1)	0.078 (1)
C13	1.1646 (3)	−0.5841 (4)	0.7919 (1)	0.068 (1)
C14	1.1149 (3)	−0.5235 (3)	0.7506 (1)	0.0532 (9)
C15	1.2520 (4)	0.0469 (4)	0.6793 (1)	0.082 (1)

Table 4. *Selected geometric parameters (Å, °) for (2)*

N1—N2	1.366 (4)	N3—C6	1.317 (5)
N1—C5	1.287 (4)	N3—C14	1.365 (4)
N2—C6	1.372 (4)	C4—C5	1.450 (5)
N2—H2*n*	0.80 (6)	C6—C7	1.408 (5)
N2—N1—C5	117.5 (3)	N1—C5—C4	117.0 (3)
N1—N2—C6	120.8 (4)	N2—C6—N3	114.7 (3)
N1—N2—H2*n*	127 (1)	N2—C6—C7	121.8 (4)
C6—N2—H2*n*	112 (1)	N3—C6—C7	123.6 (3)
C6—N3—C14	118.1 (3)		

Compound (3)

Crystal data

$C_{14}H_{10}BrN_3S$
M_r = 332.22
Tetragonal
$P4_12_12$
a = 9.5850 (7) Å
c = 29.939 (4) Å
V = 2750.6 (5) Å^3
Z = 8
D_x = 1.60 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 23 reflections
θ = 10–16°
μ = 3.129 mm^{-1}
T = 293 K
Octahedral
0.40 × 0.40 × 0.40 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.26, T_{max} = 0.29
2797 measured reflections
2415 independent reflections

1809 reflections with $I > 3\sigma(I)$
R_{int} = 0.068
θ_{max} = 25°
h = 0 → 11
k = 0 → 11
l = 0 → 35
2 standard reflections
frequency: 120 min
intensity decay: −2.4%

Refinement

Refinement on F
R = 0.026
wR = 0.033
S = 1.06
1809 reflections
176 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max}$ = 0.010
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

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

	x	y	z	U_{eq}
Br	0.15789 (5)	0.10979 (4)	0.23000 (1)	0.0596 (1)
S	−0.00274 (8)	−0.00077 (9)	0.14709 (3)	0.0400 (2)
N1	−0.1164 (3)	−0.1507 (3)	0.05433 (8)	0.0393 (7)
N2	−0.1991 (3)	−0.0624 (3)	0.08000 (9)	0.0383 (7)
N3	−0.3542 (3)	−0.0818 (3)	0.01916 (8)	0.0368 (7)
C1	0.1487 (4)	0.0020 (4)	0.1779 (1)	0.0418 (9)
C2	0.2528 (4)	−0.0744 (4)	0.1607 (1)	0.046 (1)
C3	0.2086 (4)	−0.1413 (4)	0.1208 (1)	0.046 (1)
C4	0.0739 (3)	−0.1110 (4)	0.1087 (1)	0.0371 (8)
C5	0.0078 (4)	−0.1688 (4)	0.0698 (1)	0.0395 (9)
C6	−0.3184 (3)	−0.0353 (4)	0.0607 (1)	0.0366 (8)
C7	−0.4201 (4)	0.0484 (4)	0.0831 (1)	0.046 (1)
C8	−0.5473 (4)	0.0673 (4)	0.0658 (1)	0.052 (1)
C9	−0.5880 (3)	0.0069 (4)	0.0242 (1)	0.0402 (9)
C10	−0.7219 (4)	0.0130 (4)	0.0064 (1)	0.050 (1)
C11	−0.7543 (4)	−0.0492 (4)	−0.0332 (1)	0.054 (1)
C12	−0.6513 (4)	−0.1201 (4)	−0.0568 (1)	0.051 (1)
C13	−0.5179 (4)	−0.1310 (3)	−0.0403 (1)	0.0407 (9)
C14	−0.4865 (3)	−0.0679 (3)	0.0003 (1)	0.0349 (8)

Table 6. *Selected geometric parameters (Å, °) for (3)*

N1—N2	1.391 (4)	N3—C14	1.395 (5)
N1—C5	1.289 (5)	N3—H3*n*	0.74 (7)
N2—C6	1.308 (5)	C4—C5	1.436 (5)
N3—C6	1.365 (4)	C6—C7	1.429 (6)
N2—N1—C5	114.2 (3)	N1—C5—C4	130.3 (3)
N1—N2—C6	112.0 (3)	N2—C6—N3	123.9 (3)
C6—N3—C14	124.5 (3)	N2—C6—C7	120.0 (3)
C6—N3—H3*n*	116 (1)	N3—C6—C7	116.1 (3)
C14—N3—H3*n*	118 (1)		

Compound (4)

Crystal data

$C_{14}H_{10}ClN_3S$
M_r = 287.77
Orthorhombic
$P2_12_12_1$
a = 4.6689 (8) Å
b = 11.603 (1) Å
c = 23.744 (2) Å
V = 1286.3 (3) Å^3
Z = 4
D_x = 1.49 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–16°
μ = 0.447 mm^{-1}
T = 293 K
Plate
0.53 × 0.36 × 0.23 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1362 measured reflections
1362 independent reflections
1181 reflections with $I > 3\sigma(I)$

θ_{max} = 25°
h = 0 → 5
k = 0 → 13
l = 0 → 28
2 standard reflections
frequency: 120 min
intensity decay: −1.4%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.038$
$S = 1.38$
1181 reflections
176 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{\max} = 0.088$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (4)*

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

	x	y	z	$U_{\rm eq}$
Cl	−0.9043 (2)	−0.15314 (6)	0.74016 (3)	0.0618 (2)
S	−0.5302 (2)	−0.04750 (5)	0.65314 (3)	0.0442 (2)
N1	−0.1458 (5)	0.0833 (2)	0.57763 (8)	0.0367 (5)
N2	0.0356 (5)	0.1315 (2)	0.53941 (8)	0.0371 (5)
N3	0.3733 (4)	0.1075 (2)	0.46997 (8)	0.0328 (4)
C1	−0.7536 (6)	−0.0333 (2)	0.7100 (1)	0.0408 (6)
C2	−0.7877 (6)	0.0766 (2)	0.7266 (1)	0.0450 (7)
C3	−0.6292 (6)	0.1528 (2)	0.6929 (1)	0.0425 (6)
C4	−0.4773 (6)	0.1003 (2)	0.6515 (1)	0.0360 (6)
C5	−0.2852 (5)	0.1493 (2)	0.6104 (1)	0.0372 (6)
C6	0.1862 (5)	0.0592 (2)	0.50446 (9)	0.0324 (5)
C7	0.1366 (6)	−0.0621 (2)	0.5067 (1)	0.0410 (6)
C8	0.2750 (6)	−0.1307 (2)	0.4706 (1)	0.0443 (6)
C9	0.4727 (6)	−0.0844 (2)	0.4315 (1)	0.0374 (6)
C10	0.6224 (7)	−0.1506 (2)	0.3914 (1)	0.0483 (7)
C11	0.8127 (7)	−0.1010 (3)	0.3558 (1)	0.0523 (8)
C12	0.8599 (6)	0.0175 (3)	0.3579 (1)	0.0498 (7)
C13	0.7153 (6)	0.0852 (2)	0.3956 (1)	0.0415 (6)
C14	0.5170 (5)	0.0369 (2)	0.43350 (9)	0.0332 (5)

Table 8. *Selected geometric parameters (Å, °) for (4)*

N1—N2	1.362 (3)	N3—C6	1.322 (3)
N1—C5	1.271 (3)	N3—C14	1.368 (3)
N2—C6	1.374 (3)	C4—C5	1.442 (4)
N2—H2*n*	0.88 (5)	C6—C7	1.427 (4)
N2—N1—C5	118.6 (2)	N1—C5—C4	119.7 (2)
N1—N2—C6	118.0 (2)	N2—C6—N3	117.0 (2)
N1—N2—H2*n*	116 (1)	N2—C6—C7	119.8 (2)
C6—N2—H2*n*	124 (1)	N3—C6—C7	123.2 (2)
C6—N3—C14	117.5 (2)		

Procedures for crystal orientation, unit-cell determination and refinement and data collection have been published previously (Mague & Lloyd, 1989). For (1) and (4), the space groups were uniquely determined by the observed systematic absences, while for (2) and (3), the absences indicated $P4_12_12$ and $P4_32_12$ as possible choices. E maps calculated for (1) and (4) provided positions for virtually all non-H atoms and all H atoms were located in $\Delta\rho$ maps in the late stages of the refinement. All H atoms were refined in (1), while in (4), only that attached to N was refined with the remainder included as fixed contributions and updated periodically. Following convergence for (4), the opposite enantiomorph was also refined leading to a significant (>95% confidence level) improvement in the agreement factors so the latter was taken as the correct model. For (3), the largest peak observed in the E map calculated in $P4_12_12$ was taken to be a Br atom and from this, the full structure was developed by successive cycles of refinement followed by calculation of a $\Delta\rho$ map. All H atoms could be located and were treated as for (4). As both quinolyl ring atoms bound to C6 in (3) had attached H atoms, the position of N3, initially chosen to be the same relative to sulfur as found in (1), (2) and (4), was checked by interchanging the identities of C7 and N3. This choice gave unreasonable displacement parameters for both atoms indicating the original choice to be correct. Following convergence in $P4_12_12$, the model was refined in $P4_32_12$ which resulted in significantly (>95% confidence level) poorer agreement factors indicating the initial choice to be correct. Attempts to solve (2) in either of the possible space groups were unsuccessful. Ultimately, a solution was obtained, using the full octant of data collected and the orthorhombic space group $P2_12_12_1$ with $Z = 8$, from which it became clear that the two 'independent' molecules were related by a twofold axis. Inspection of the positional parameters so obtained for the set of eight S atoms showed that they could be readily fitted to the eightfold general position of $P4_32_12$ (but not to $P4_12_12$) by the transformation $(x, y, z) \rightarrow (\frac{1}{4} + x, y, \frac{1}{8} + z)$. Refinement proceeded uneventfully from this point with the H atoms being treated as for (4).

For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *PROCESS* in *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* (direct methods; Burla *et al.*, 1989); program(s) used to refine structure: *LSFM* in *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN*.

The authors thank the Chemistry Department of Tulane University for generous financial support of the X-ray diffraction facility. Support from the Faculty Development Program (to DGB) and the Undergraduate Collaboration Grant Program (to WFW and SV) at the University of Wisconsin Oshkosh is also gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1314). Services for accessing these data are described at the back of the journal.

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(6Z,8Z)-2,4,6-Trimethyl-8-phenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione

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(Received 24 October 1996; accepted 14 February 1997)

Abstract

The title compound, $C_{14}H_{16}N_2O_3$, is a model of the crucial intermediate in a postulated mechanism for the enzyme (6–4) photoproduct photolyase, which repairs a particular form of UV-light induced DNA damage. The dihedral angle of the two oxetane ring H atoms is 143.5°, which means the bulky phenyl ring is *exo* to the pyrimidine ring.

Comment

Ultraviolet (UV) light is responsible for many forms of damage to DNA, which includes strand breaks, formation of abasic sites, base hydrolysis and the dimerization of adjacent bases. The most common form of the latter type of damage is the dimerization of adjacent thymines on the same DNA strand (Friedberg, 1985). In the presence of UV light, the two pyrimidines can form either a cyclobutane dimer (CBD), or a (6–4) dimer (Cadet, Anselmino, Douki & Voituriez, 1992). The CBD is the more prevalent of the two photoproducts, and therefore has been studied extensively (Wulff & Fraenkel, 1961; Ragini, 1965; Gangamani, Cheravakkattu & Ganesh, 1994). In organisms such as *E. coli*, *D. melanogaster*, and *X. laevis* this damage is repaired, in the presence of light, by CBD photolyase (Sancar, 1994). On the other hand, the (6–4) dimer is relatively poorly understood. This photoproduct is postulated to form after an initial Paterno–Büchi reaction between the 5,6-double bond of the 5′-thymine, and the C-4 carbonyl of the 3′-thymine, followed by a ring opening of the subsequent oxetane (Varghese & Wang, 1968).

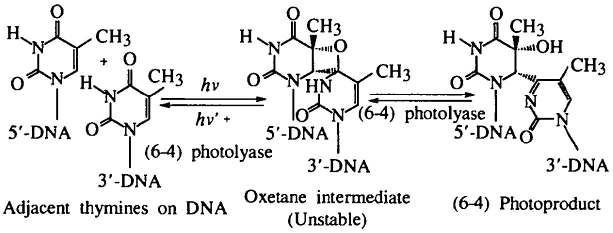

Fig. 1. Formation of the (6–4) photoproduct between two thymines in DNA.

The (6–4) dimer is repaired by the enzyme (6–4) photoproduct photolyase (Todo *et al.*, 1993). A mechanism has been proposed for this enzyme, which is as follows: the enzyme binds to the damaged part and first converts the (6–4) dimer to the oxetane, then, in the presence of light, and certain electron-rich enzyme cofactors, (6–4) photolyase breaks the oxetane ring to yield the two parent thymines (Kim, Malhotra, Smith, Taylor & Sancar, 1994). Unfortunately, the postulated oxetane intermediate between two thymines is unstable above 193 K (Rahn & Hosszu, 1969), and is unhelpful in the support of this mechanism. On the other hand, various stable thietanes between adjacent thymidines have been synthesized and characterized (Clivio, Fourrey, Gasche & Farve, 1992; Liu & Taylor, 1996).

In order to test this proposed mechanism, we have prepared an oxetane of 1,3-dimethylthymine (DMT) with benzaldehyde, and have shown that this oxetane, (I), can be split into its constituent parts in the presence of light, and a variety of electron-donating and electron-accepting sensitizers (Prakash & Falvey, 1995). Unlike the 'natural' oxetane, this compound is stable at room temperature. Although the actual mechanism of (6–4) photoproduct photolyase is still under investigation, our results are consistent with the proposed mechanism (Kim, Malhotra, Smith, Taylor & Sancar, 1994). In