

(Z)-6-[[1,3-Dihydroxy-2-(hydroxymethyl)propan-2-ylamino]methylene]-2-methoxy-4-{(E)-[3-(trifluoromethyl)phenyl]diazanyl}cyclohexa-2,4-dienone**Cem Cüneyt Ersanlı,^{a*} Çiğdem Albayrak,^b Mustafa Odabaşoğlu^b and Canan Kazak^a**^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey, and ^bDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit Samsun, Turkey

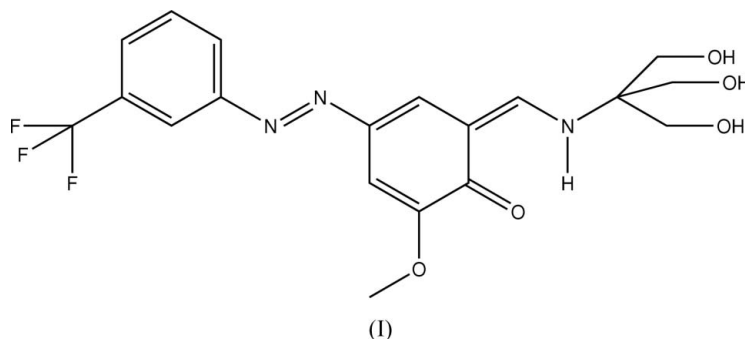
Correspondence e-mail: ccersan@omu.edu.tr

Key indicatorsSingle-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.033
 wR factor = 0.086
Data-to-parameter ratio = 11.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The molecule of the title compound, $\text{C}_{19}\text{H}_{20}\text{F}_3\text{N}_3\text{O}_5$, at 150 K, is nearly planar and exists in the keto–amine ($\text{N}-\text{H}\cdots\text{O}$) tautomeric form, with a strong intramolecular hydrogen bond of 2.585 (2) Å between the O and N atoms. The configuration around the azo $-\text{N}=\text{N}-$ double bond is *trans*, as found for other diazene derivatives, and the dihedral angle between the planes of the two aromatic rings is 7.81 (4)°.

Comment

Optically active azobenzene polymers are very important functional materials because of their photoresponsive properties. The pendant azobenzene groups in these materials behave as both photoresponsive chromophores and mesogens (Labarthe *et al.*, 1999). Recently, the formation of holographic gratings with polymeric azobenzene liquid crystals (LC) containing only azobenzene groups, where each group is mesogenic and photoresponsive, was reported (Yamamoto *et al.*, 2001).



There is considerable interest in Schiff base ligands and their complexes with regard to their striking antitumour activities (Zhou *et al.*, 2000). Among them, *o*-hydroxy Schiff base ligands and their complexes derived from the reaction of *o*-hydroxyaldehydes with aniline have been extensively studied (Stewart & Lingafelter, 1959; Calligaris *et al.*, 1972; Maslen & Waters, 1975) and a number of these compounds have been used as models for biological systems (Costamagna *et al.*, 1992, 1998). *o*-Hydroxy Schiff bases have previously been observed in the keto form (Ersanlı *et al.*, 2003; Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez, 2004), in the enol form (Ersanlı, Odabaşoğlu *et al.*, 2004a; Ersanlı, Albayrak, Odabaşoğlu & Erdönmez, 2004) or in enol/keto mixtures (Nazır *et al.*, 2000), by means of H-atom transfer. Related to this phenomenon, we present here the structure of the title compound, (I).

The C11–O2 and C15–N3 bond lengths verify the keto–amine form of compound (I) (Table 1 and Fig. 1). These

Received 25 October 2005

Accepted 31 October 2005

Online 10 November 2005

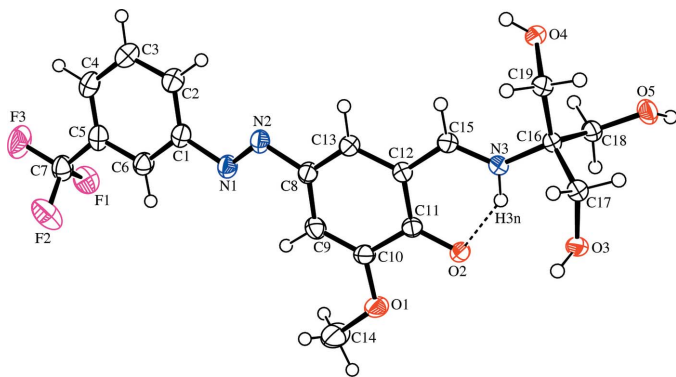


Figure 1
A view of the molecule of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

distances agree with the corresponding distances in 4-[(2-chlorophenyl)diazenyl]-6-methoxy-2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one [1.287 (2) and 1.294 (2) Å; Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez, 2004], which also shows the keto–amine tautomeric form. The same bonds can be compared with the corresponding distances in 2-[2-(hydroxymethyl)phenyliminomethyl]phenol [1.354 (2) and 1.275 (2) Å; Ersanlı, Odabaşoğlu *et al.*, 2004a] and 4-(2-hydroxyphenyliminomethylene)phenol [1.355 (2) and 1.278 (2) Å; Ersanlı, Albayrak, Odabaşoğlu & Erdönmez, 2004], which exist in the enol–imine tautomeric form.

In the azo group of (I), the C1–N1 and N2–C8 bond lengths [1.426 (2) and 1.411 (2) Å, respectively] indicate significant single-bond character, whereas the –N=N– bond length [1.264 (2) Å] is indicative of significant double-bond character. Similar values have been observed in other *trans*-azo compounds (Ersanlı, Odabaşoğlu *et al.*, 2004b; Ersanlı, Albayrak, Odabaşoğlu, Kazak & Erdönmez, 2004). The dihedral angle between the mean planes of the C1–C6 benzene ring and the C1–N1=N2–C8 azo bridge is 8.36 (7)°, and the angle between the planes of the C1–N1=N2–C8 azo group and the C8–C13 benzene ring is 8.20 (5)°. The angle between the two benzene rings is 7.81 (4)°.

There is a strong intramolecular N3–H3n···O2 hydrogen bond (Table 2), with the H atom transferred from the O to the N atom. The N3···O2 distance [2.585 (2) Å] is shorter than the sum of the van der Waals radii of O and N [3.07 Å; Bondi *et al.*, 1964] and comparable with the distances observed in 4-[(2-chlorophenyl)diazenyl]-6-methoxy-2-[[tris(hydroxymethyl)methyl]aminomethylene]cyclohexa-3,5-dien-1(2*H*)-one [2.584 (2) Å; Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez, 2004]. Each molecule also participates in O–H···O hydrogen bonds (Table 2 and Fig. 2).

Experimental

Compound (I) was prepared using *o*-vanillin, 3-(trifluoromethyl)aniline and tris(hydroxymethyl)aminomethane as starting materials (Ersanlı, Albayrak, Odabaşoğlu, Thöne & Erdönmez,

2004). A mixture of 3-(trifluoromethyl)aniline (1.61 g, 10 mmol), water (50 ml) and concentrated hydrochloric acid (2.5 ml, 30 mmol) was heated with stirring until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (0.96 g, 14 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. *o*-Vanillin (1.22 g, 10 mmol) solution (pH 9) was gradually added to a cooled solution of 3-(trifluoromethyl)benzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273–278 K for 60 min in an ice bath. The product was recrystallized from ethyl alcohol to obtain solid 3-methoxy-5-[3-(trifluoromethyl)phenylazo]salicylaldehyde. To a solution of this solid (1.74 g, 5 mmol) in butan-1-ol (75 ml) was added a solution of tris(hydroxymethyl)aminomethane (0.605 g, 5 mmol) in butan-1-ol (25 ml). The mixture was stirred under reflux and the water produced in the reaction was distilled out. The resulting red precipitate was filtered off and recrystallized from ethyl alcohol. Crystals of (I) were obtained after 2 d by slow evaporation from acetonitrile (yield 77%; m.p. 518–519 K).

Crystal data

C₁₉H₂₀F₃N₃O₅

M_r = 427.38

Monoclinic, *P*2₁/*c*

a = 16.4030 (13) Å

b = 10.3467 (5) Å

c = 11.4251 (9) Å

β = 100.052 (6)°

V = 1909.3 (2) Å³

Z = 4

D_x = 1.487 Mg m^{−3}

Mo *K*α radiation

Cell parameters from 12935

reflections

θ = 1.8–27.3°

μ = 0.13 mm^{−1}

T = 150 (2) K

Prism, red

0.36 × 0.31 × 0.20 mm

Data collection

Stoe IPDS-II diffractometer

ω scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

T_{min} = 0.955, *T_{max}* = 0.972

17660 measured reflections

4187 independent reflections

3278 reflections with *I* > 2σ(*I*)

R_{int} = 0.028

θ_{max} = 27.1°

h = −17 → 20

k = −13 → 13

l = −14 → 14

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.033

wR(*F*²) = 0.086

S = 1.04

4187 reflections

351 parameters

All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0438*P*)² + 0.2797*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.22 e Å^{−3}

Δρ_{min} = −0.19 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

F1–C7	1.343 (2)	O1–C10	1.361 (2)
F2–C7	1.336 (2)	O1–C14	1.419 (2)
F3–C7	1.330 (2)	O2–C11	1.2806 (15)
N1–N2	1.264 (2)	O3–C17	1.429 (1)
N1–C1	1.426 (2)	O4–C19	1.419 (2)
N2–C8	1.411 (2)	O5–C18	1.414 (2)
N3–C15	1.291 (2)		
N1–N2–C8	113.42 (10)	N3–C15–C12	121.68 (11)
O2–C11–C12	123.37 (11)	C15–N3–C16	129.84 (10)
O2–C11–C10	120.14 (11)		
C1–N1–N2–C8	−178.75 (10)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N \cdots O2	0.89 (2)	1.82 (2)	2.585 (2)	143 (2)
O3—H3O \cdots O4 ⁱ	0.82 (2)	1.89 (2)	2.712 (1)	177 (2)
O4—H4O \cdots O2 ⁱⁱ	0.78 (2)	2.02 (2)	2.751 (1)	157 (2)
O4—H4O \cdots O1 ⁱⁱ	0.78 (2)	2.26 (2)	2.804 (1)	128 (2)
O5—H5O \cdots O3 ⁱⁱⁱ	0.83 (2)	1.90 (2)	2.731 (1)	174 (2)

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

All H atoms were refined isotropically. The refined C—H and O—H bond lengths are in the ranges 0.96 (2)–1.01 (2) and 0.78 (2)–0.83 (2) Å, respectively. The N3—H3N bond length is 0.89 (2) Å.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS II diffractometer (purchased under grant No. F279 of the University Research Fund).

References

- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Calligaris, M., Nardin, G. & Randaccio, L. (1972). *Coord. Chem. Rev.* **7**, 385–403.
- Costamagna, J., Barroso, N. P., Matsuhira, B. & Villagrán, M. (1998). *Inorg. Chim. Acta*, **273**, 191–195.
- Costamagna, J., Vargas, J., Latorre, R., Alvarado, A. & Mena, G. (1992). *Coord. Chem. Rev.* **119**, 67–88.
- Ersanlı, C. C., Albayrak, Ç., Odabaşoğlu, M. & Erdönmez, A. (2003). *Acta Cryst.* **C59**, o601–o602.
- Ersanlı, C. C., Albayrak, Ç., Odabaşoğlu, M. & Erdönmez, A. (2004). *Acta Cryst.* **E60**, o389–o391.
- Ersanlı, C. C., Albayrak, Ç., Odabaşoğlu, M., Kazak, C. & Erdönmez, A. (2004). *Acta Cryst.* **C60**, o455–o457.
- Ersanlı, C. C., Albayrak, Ç., Odabaşoğlu, M., Thöne, C. & Erdönmez, A. (2004). *Acta Cryst.* **C60**, o133–o135.
- Ersanlı, C. C., Odabaşoğlu, M., Albayrak, Ç. & Erdönmez, A. (2004a). *Acta Cryst.* **E60**, o264–o266.
- Ersanlı, C. C., Odabaşoğlu, M., Albayrak, Ç. & Erdönmez, A. (2004b). *Acta Cryst.* **E60**, o230–o231.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Labarthe, F. L., Rochon, P. & Natansohn, A. (1999). *Appl. Phys. Lett.* **75**, 1377–1379.
- Maslen, H. S. & Waters, T. N. (1975). *Coord. Chem. Rev.* **17**, 137–176.
- Nazır, H., Yıldız, M., Yılmaz, H., Tahir, M. N. & Ülkü, D. (2000). *J. Mol. Struct.* **524**, 241–250.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stewart, J. M. & Lingafelter, E. C. (1959). *Acta Cryst.* **12**, 842–845.
- Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
- Yamamoto, T., Ohashi, A., Yoneyama, S., Hasegawa, M., Tsutsumi, O., Kanazawa, A., Shiono, T. & Ikeda, T. (2001). *J. Phys. Chem. B*, **105**, 2308–2313.
- Zhou, Y.-S., Zhang, L.-J., Zeng, X.-R., Vital, J. J. & You, X.-Z. (2000). *J. Mol. Struct.* **524**, 241–250.

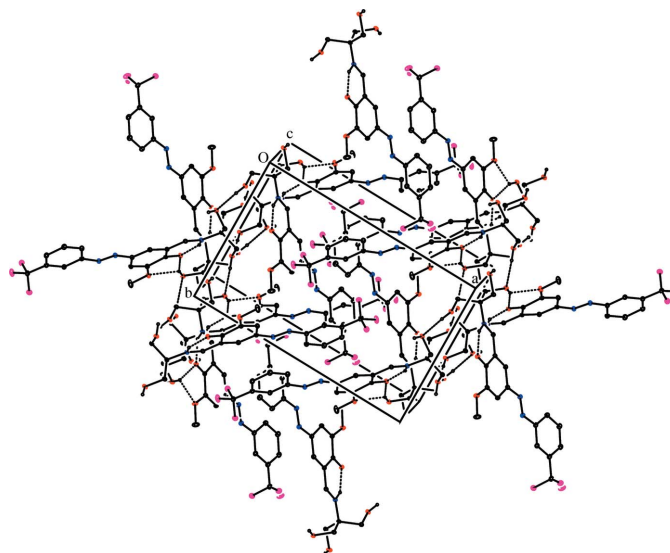


Figure 2
Part of the crystal packing of (I). Hydrogen bonds are drawn as dashed lines. For the sake of clarity, all H atoms, except for H3N, H3O, H4O and H5O, have been omitted.