Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Doyle, I. R. & Massy-Westropp, R. A. (1982). *Aust J. Chem.* **35**, 1903–1911.
Kayser, M. M. & Breau, L. (1988). *Tetrahedron Lett.* **29**, 6203–6206.
Kayser, M. M. & Breau, L. (1989). *Can. J. Chem.* **67**, 1401–1410.
Kayser, M. M., Hatt, K. L. & Hooper, D. L. (1991). *Can. J. Chem.* **69**, 1929–1939.
Kayser, M. M., Hatt, K. L. & Hooper, D. L. (1992). *Can. J. Chem.* **70**, 1985–1996.
Kayser, M. M., Hatt, K. L., Yu, H. & Hooper, D. L. (1993). *Can. J. Chem.* **71**, 1010–1021.
Knight, D. W. & Pattenden, G. (1975). *J. Chem. Soc. Perkin. Trans.* 1, pp. 635–640.
Knight, D. W. & Pattenden, G. (1979). *J. Chem. Soc. Perkin. Trans.* 1, pp. 62–76, 84–88.
Melanson, R. & Rochon, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.
Pattenden, G. (1978). *Fortschr. Chem. Org. Naturst.* **35**, 1–197.
Sheldrick, G. M. (1984). *SHELXTL User's Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

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2,2′-Azinodimethyldiphenol, $C_{14}H_{12}N_2O_2$

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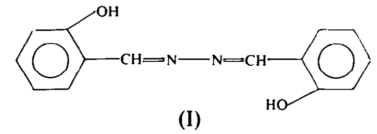
Abstract

The X-ray single-crystal structure determination of the title compound reveals a *trans* planar structure in which the molecules stack in columns parallel to the *c* axis of the unit cell. Each molecule contains intramolecular O···N hydrogen bonds [2.611 (6) Å].

Comment

Proton transfer, accompanied by a configurational change of the π-electron structure, is one of the key reactions in many proposals for molecular-electronic devices. Schiff base compounds undergo photochromism and thermochromism in the solid state by proton transfer from the hydroxyl O atom to the imine N atom, which may be reversible. Molecular switches may also be based on proton transfer. In the molecular systems, with proton transfer, the charge transport occurs through overlapping intermolecular π orbitals. The electrical properties depend heavily on the intermolecular interactions. Thus, a thermochromic Schiff base may be a candidate for construction of a novel type of conductive organic material in which the proton motion is essentially correlated to the electron conduction (Hadjoudis, Vittorakis, Moustakali-Mavridis, 1987; Inabe, 1991). These phenomena may be related to the molecular packing in the lattice (Bregman, Leiserowitz & Schmidt, 1964). In this paper, the structure of the title compound, (I), is described.



(I)

The molecular geometry is illustrated in Fig. 1. The molecule is located on the centre of inversion so that only one half of the molecule is crystallographically independent. The N—C(7) [1.285 (7) Å] and N—N′ [1.386 (9) Å] distances indicate that these correspond to double and single bonds, respectively. Although the bond length O—H(O) is typical of a hydroxyl group, the distance between the O and N atoms, which are intramolecularly hydrogen bonded, is 2.611 (6) Å, and is comparable to those observed for thermochromic *N*,*N*′-disalicylidene-1,6-pyrenediamine [2.614 Å (Inabe, Hoshino, Mitani & Maruyama, 1989)] and photochromic 2-chloro-*N*-salicylideneaniline [2.609 Å (Bregman, Leiserowitz & Osaki, 1964)]. The O—C(1) bond length [1.364 (8) Å] is in the range observed for other *N*-salicylideneanilines (Inabe, Hoshino, Mitani & Maruyama, 1989; Bregman, Leiserowitz & Osaki, 1964; Bregman, Leiserowitz & Schmidt, 1964). The torsion angles N—C(7)—C(6)—C(1) [−2.61 (7)°] and N—C(7)—C(6)—C(5) [179.51 (7)°] indicate that the molecule is practically planar. The maximum deviation from the mean plane is 0.016 Å for non-H atoms. The molecules stack tightly to form columns

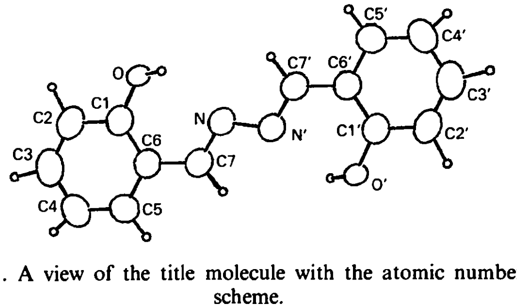


Fig. 1. A view of the title molecule with the atomic numbering scheme.

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parallel to the *c* axis (See Fig. 2). In thermochromic Schiff base compounds, this planar structure makes it possible for the proton to transfer through the hydrogen bond in the ground state with a small energy requirement (Bregman, Leiserowitz & Osaki, 1964; Bregman, Leiserowitz & Schmidt, 1964).

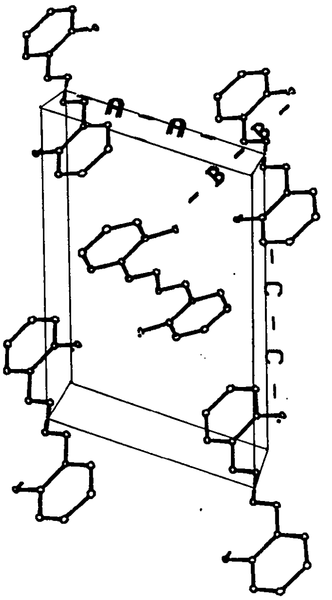

Fig. 2. A view of the unit cell of the crystal.

Experimental

The title compound was prepared by condensation of hydrazine hydrate and salicylaldehyde in a 1:2 molar ratio in ethanol.

Crystal data

$C_{14}H_{12}N_2O_2$
$M_r = 240.26$
Monoclinic
$P2_1/n$
$a = 8.518$ (1) Å
$b = 6.305$ (1) Å
$c = 11.812$ (2) Å
$\beta = 107.92$ (1)°
$V = 603.6$ Å^3
$Z = 2$
$D_x = 1.32$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 8$–19°
$\mu = 0.7$ mm^{-1}
$T = 296$ K
Needle
$0.20 \times 0.20 \times 0.20$ mm
Pale yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans [1-10° min^{-1}; width $(0.50 + 0.140\tan\theta)$° in ω]
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.985$, $T_{\max} = 0.998$
1111 measured reflections
849 independent reflections

795 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.014$
$\theta_{\max} = 64$°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 13$
2 standard reflections
frequency: 90 min
intensity variation: 0.9%

Refinement

Refinement on F
$R = 0.071$
$wR = 0.073$
$S = 0.67$
795 reflections
102 parameters
H atoms refined with fixed $B_{\rm iso} = 5.0$ Å^2

$(\Delta/\sigma)_{\max} = 0.45$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$B_{\rm iso}$ for H atoms; $B_{\rm eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for N, C and O.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
N	0.4973 (4)	0.4167 (6)	0.4612 (3)	4.10 (8)
C(1)	0.5150 (6)	0.0514 (7)	0.3225 (4)	4.6 (1)
C(2)	0.5321 (6)	−0.1308 (8)	0.2600 (4)	5.2 (1)
C(3)	0.6654 (7)	−0.2559 (8)	0.3029 (4)	5.7 (1)
C(4)	0.7883 (6)	−0.2114 (8)	0.4080 (5)	5.3 (1)
C(5)	0.7690 (6)	−0.0319 (7)	0.4716 (4)	4.7 (1)
C(6)	0.6339 (5)	0.1021 (7)	0.4283 (3)	3.96 (9)
C(7)	0.6191 (6)	0.2877 (7)	0.4979 (4)	4.21 (9)
O	0.3794 (5)	0.1753 (7)	0.2746 (3)	3.91 (9)
H2	0.437 (8)	−0.15 (1)	0.192 (5)	5.0
H3	0.676 (8)	−0.39 (1)	0.257 (5)	5.0
H4	0.888 (8)	−0.35 (1)	0.385 (5)	5.0
H5	0.835 (8)	0.00 (1)	0.545 (5)	5.0
H7$^{\rm i}$	0.700 (9)	0.32 (1)	0.576 (5)	5.0
H(O)	0.3898	0.3225	0.2785	5.0

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

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

N—N′	1.386 (9)	C(3)—C(4)	1.38 (2)
N—C(7)	1.285 (7)	C(4)—C(5)	1.396 (9)
C(1)—C(2)	1.398 (8)	C(5)—C(6)	1.393 (9)
C(1)—C(6)	1.382 (8)	C(6)—C(7)	1.457 (7)
C(1)—O	1.364 (8)	N···O	2.611 (6)
C(2)—C(3)	1.35 (2)		
N—N′—C(7)	113.4 (6)	C(3)—C(4)—C(5)	117.7 (6)
C(2)—C(1)—C(6)	120.1 (6)	C(1)—C(6)—C(5)	119.1 (5)
C(2)—C(1)—O	117.7 (5)	C(1)—C(6)—C(7)	121.9 (6)
C(6)—C(1)—O	122.2 (6)	C(5)—C(6)—C(7)	119.0 (6)
C(1)—C(2)—C(3)	119.8 (7)	N—C(7)—C(6)	121.3 (5)
C(2)—C(3)—C(4)	122.4 (7)		

The structure was solved by direct methods and a difference Fourier synthesis and refined with unit weights by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms and fixed isotropic displacement parameters for H atoms. All calculations were performed on a PDP 11/44 computer with the Enraf-Nonius *SDP* program package (Frenz, 1978). *PLUTO* (Motherwell & Clegg, 1978) was used for generation of molecular graphics.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bregman, J., Leiserowitz, L. & Osaki, K. (1964). *J. Chem. Soc.* pp. 2086–2100.

Bregman, J., Leiserowitz, L. & Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Hadjoudis, E., Vittorakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.

Inabe, T. (1991). *New J. Chem.* **15**, 129–136.

Inabe, T., Hoshino, N., Mitani, T. & Maruyama, Y. (1989). *Bull. Chem. Soc. Jpn*, **42**, 2245–2251.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

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3,4-Diméthoxycarbonyl-5-éthoxycarbonyl-1-(2,2,2-trichloro-1-éthoxycarbonylaminoéthyl)pyrazole, $C_{15}H_{18}Cl_3N_3O_8$

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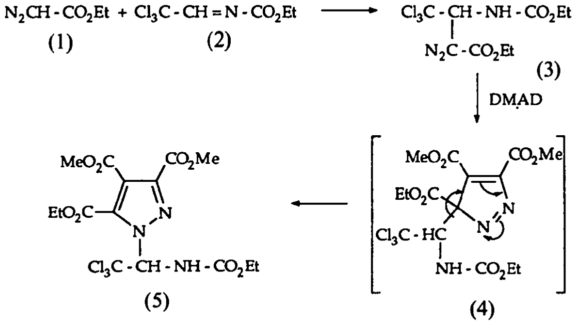
Abstract

The part of the molecule of 5-ethyl 3,4-dimethyl 1-[2,2,2-trichloro-1-(ethoxycarbonylamino)ethyl]-pyrazole-3,4,5-tricarboxylate containing the pyrazole ring, the 5-ethoxycarbonyl and the 3-methoxycarbonyl substituents is approximately planar. The least-squares plane of the pyrazole ring makes angles of 90.5 (2)° with the 4-methoxycarbonyl group and 111.0 (2)° with the plane of the carbonylamino group. An intramolecular N—H···Cl hydrogen bond [3.003 (4) Å, 103 (3)°] forms a pseudo-cycle. The crystal structure is composed of dimers, the molecules of a dimer being linked together by two N—H···O hydrogen bonds [3.034 (5) Å, 163 (4)°].

Commentaire

Le produit attendu, au terme de la préparation représentée par le schéma ci-dessous [composé (4)], résulte de l'action de l'acétylène dicarboxylate de diméthyle (DMAD) sur le 4,4,4-trichloro-3-éthoxycarbonylamino-2-diazobutyrate d'éthyle (3) lui-même obtenu à partir du diazoacétate d'éthyle (1) et de la *N*-éthoxycarbonyl-*N*-(2,2,2-trichloroéthylidène)amine (2). La molécule de (4) contient deux atomes de C asymétriques. Aussi l'objectif assigné à l'étude cristallographique fut-il de déterminer les conformations relatives de ces deux atomes. En fait, ce travail a montré que le produit soumis à l'analyse structurale est le composé (5) dont la molécule contient un seul centre d'asymétrie. Il a aussi permis de proposer un mécanisme pour expliquer sa formation à partir de (4) *via* une transposition sigmatropique [1,5] du groupe 2,2,2-trichloro-1-éthoxycarbonylaminoéthyle.



Les coordonnées atomiques relatives et les facteurs de température isotropes équivalents sont rapportés dans le Tableau 1, les longueurs et les angles des liaisons dans le Tableau 2. Les noms des atomes sont indiqués sur la Fig. 1.

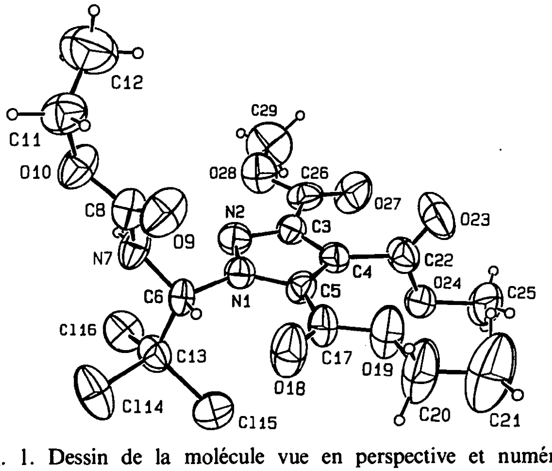


Fig. 1. Dessin de la molécule vue en perspective et numéros attribués à ses atomes.