C4	0.4206 (4)	0.8087 (3)	0.4540 (2)	0.0640 (12)
C5	0.3481 (4)	0.7625 (3)	0.5187 (2)	0.0600 (11)
C6	0.2776 (4)	0.6209 (3)	0.5239 (2)	0.0501 (10)
C7	0.1979 (3)	0.3738 (3)	0.47329 (13)	0.0410 (8)
C8	0.0658 (3)	0.0377 (3)	0.38916 (12)	0.0433 (9)
C9	−0.0372 (4)	−0.3490 (3)	0.27748 (14)	0.0540 (10)
C10	−0.0993 (5)	−0.4960 (3)	0.2465 (2)	0.087 (2)

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

C2—O2	1.352 (3)	C2—C1	1.390 (3)
C8—O8*a*	1.247 (3)	C6—C1	1.397 (3)
C8—N8*b*	1.327 (3)	C7—C1	1.450 (3)
C9—O9*a*	1.202 (3)	C3—C2	1.389 (4)
C9—O9*b*	1.301 (3)	C4—C3	1.368 (4)
N8—N7	1.378 (3)	C5—C4	1.372 (5)
C7—N7	1.279 (3)	C6—C5	1.369 (4)
C8—N8	1.345 (3)	C10—C9	1.494 (4)
N8—N7—C7	115.3 (2)	C6—C5—C4	119.4 (3)
C8—N8—N7	122.2 (2)	C1—C6—C5	121.7 (3)
C2—C1—C6	117.8 (2)	N7—C7—C1	123.4 (2)
C6—C1—C7	119.3 (2)	O8*a*—C8—N8*b*	123.0 (2)
C7—C1—C2	122.9 (2)	O8*a*—C8—N8	118.3 (2)
C3—C2—O2	117.2 (2)	N8*b*—C8—N8	118.6 (2)
C3—C2—C1	120.3 (2)	C10—C9—O9*a*	124.3 (3)
O2—C2—C1	122.5 (2)	C10—C9—O9*b*	112.8 (3)
C4—C3—C2	120.1 (3)	O9*a*—C9—O9*b*	122.8 (2)
C5—C4—C3	120.7 (3)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O2—H2···N7	0.90 (3)	1.93 (3)	143 (3)
O2—H2···O9*a*$^{\rm i}$	0.90 (3)	2.47 (3)	104 (2)
N8*b*—H8*a*···O9*a*	0.88 (3)	2.37 (3)	158 (3)
N8*b*—H8*a*···O2*a*$^{\rm ii}$	0.88 (3)	2.42 (3)	126 (3)
N8*b*—H8*b*···N7	0.92 (3)	2.38 (3)	102 (2)
N8*b*—H8*b*···O9*a*$^{\rm i}$	0.92 (3)	2.20 (3)	151 (2)
N8—H8···O8*a*$^{\rm iii}$	0.87 (2)	2.07 (2)	172 (2)
O9*b*—H9*b*···O8*a*	1.01 (3)	1.61 (3)	164 (3)

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

The methyl H atoms of C10 are found to be disordered. The refined structure includes two sets of idealized methyl H atoms with fixed displacement parameters. Their site-occupation factors refined to 0.60 (2) and 0.40 (2), respectively. The ω-scan width was symmetrically over 1.2° about the $\alpha_{1,2}$ maximum and the background was offset 1.0 and −1.0° in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable 3–6° min^{-1} (depending upon intensity). The linear absorption coefficient was calculated using values from the *International Tables for X-ray Crystallography* (1974).

Programs used: *SHELXTL-Plus* (Sheldrick, 1991) for cell refinement, data collection, data reduction, structure solution (direct methods) and molecular graphics, and *SHELX76* (Sheldrick, 1976) for structure refinement (full-matrix least-squares).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and bond distances and angles involving H atoms have been deposited with the IUCr (Reference: CR1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,5,6-Tetrachloro-4-hydroxyphenyl *N*-(4-Chlorophenyl)benzenecarboximidate

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Abstract

When 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil) is reacted with *N*-benzylidene-*p*-chloroaniline, its quinoidal structure is converted to a phenolic derivative, the title compound ($C_{19}H_{10}Cl_5NO_2$). The C—O bond distances, 1.345 (5) and 1.389 (5) Å, indicate that they are hydroxyl and ether bonds, respectively. The N—C bond lengths are 1.272 (5) and 1.433 (5) Å, which

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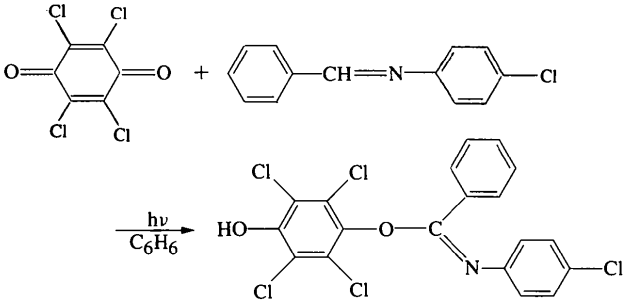
correspond to a double and single bond, respectively. The geometry of the central skeleton is distorted owing to the intramolecular phenyl–phenyl repulsions.

Comment

Although photoinduced reactions of quinones with alkenes have received extensive investigation (Maruyama, 1988; Xu, Song, Zhang, Wang & Xu, 1994), no photoinduced reactions of quinones with Schiff bases have been reported. Xu, Song, Zhang, Whang & Xu (1994) found that during the photolysis of chloranil (CA) with alkenes, the cycloaddition products, oxetane and/or cyclobutane derivatives, depended on the structure of the alkenes. On investigating the reactions of CA with Schiff bases under photoinduced conditions, substitution rather than cycloaddition was found to take place and a new kind of Schiff base, (I), was synthesized (Chen, Zhang, Yan & Xu, 1994).



The C(19)—N(1) [1.272 (5) Å] and C(7)—N(1) [1.433 (5) Å] distances indicate that they correspond to double and single bonds, respectively. These parameters are similar to those of benzylideneaniline *p*-carboxylic acid (BAC) (1.281 and 1.431 Å; Bürgi & Dunitz, 1970) and *N*-(diphenylmethylene)aniline (DPA) (1.287 and 1.420 Å; Tucker, Hoekstra, ten Cate & Vos, 1975), but are quite different from those of benzylideneaniline (BA; Bürgi & Dunitz, 1970) in which C=N is 1.237 and C—N is 1.460 Å.

The geometry of the central skeleton is distorted owing to the repulsion between C(7) and C(13). In the title compound, the C(13)—C(19)—N(1) angle [131.3 (4)°] is enlarged compared with the O(2)—C(19)—N(1) angle [118.0 (4)°]. The N atom forms an intermolecular hydrogen bond with the phenolic O(1) atom [2.88 (1) Å] which causes the C=N—C angle [121.3 (3)°] to be larger than in BA, BAC and DPA, but smaller than in triphenylnitrone (TPN) (Brown & Trefonas, 1973). The C(13)—C(19)—N(1) angle is also large [131.3 (4)°] compared with the corresponding angles in DPA and TPN (Tucker, Hoekstra, ten Cate & Vos, 1975; Brown & Trefonas, 1973).

After CA was reacted with *N*-benzylidene-*p*-chloroaniline to form the title compound, bond distances in the former quinone ring ranged from 1.365 (6) to 1.402 (6) Å, consistent with benzenoid character and significantly different from the C—C bond lengths in CA itself (Chu, Jeffrey & Sakurai, 1962). The change in the C(3)—O(1) bond distance from 1.195 Å in CA to 1.345 (5) Å in the title compound indicates that the C=O group is converted to a hydroxyl group. It can be seen that C(6)—O(2) [1.389 (5) Å] and C(19)—O(2) [1.372 (5) Å] are consistent with an ether bond. The average C—Cl bond length in the phenolic group [1.721 (5) Å] is 0.007 Å longer than that in CA.

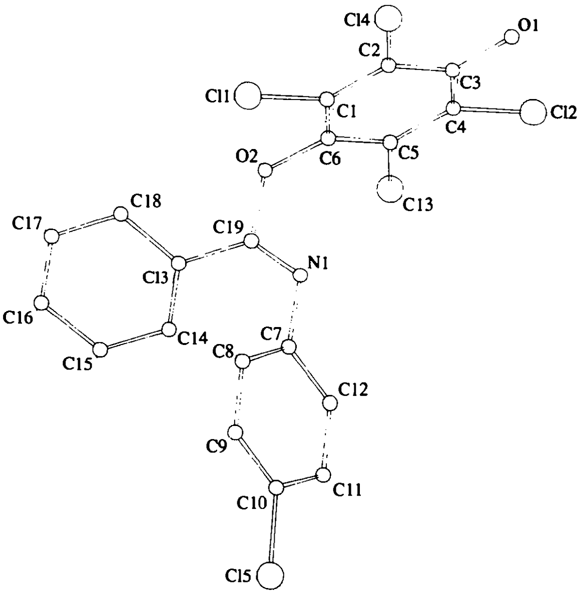


Fig. 1. The molecular geometry of the title compound.

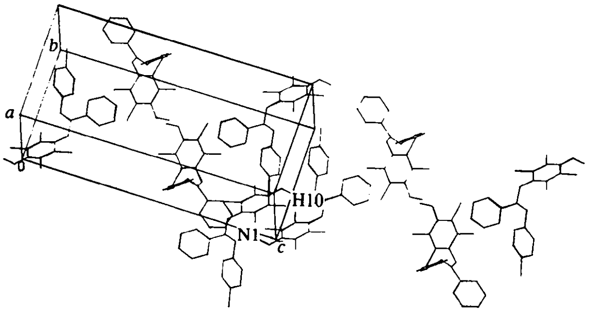


Fig. 2. The unit cell of the title compound.

Experimental

Crystal data

$C_{19}H_{10}Cl_5NO_2$
$M_r = 461.6$
Monoclinic
$P2_1/n$
$a = 7.853$ (3) Å
$b = 11.025$ (1) Å
$c = 22.708$ (5) Å
$\beta = 95.96$ (1)°

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10$–14°
$\mu = 0.76$ mm^{-1}
$T = 296$ K
Prism

$V = 1955.4$ (3) Å^3
$Z = 4$
$D_x = 1.568$ Mg m^{-3}

0.25 × 0.20 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans [width ($0.50 + 0.140\tan\theta$)° in ω, speed 1–10° min^{-1}]
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983) $T_{\min} = 0.820$, $T_{\max} = 0.999$
3917 measured reflections

3633 independent reflections
2156 observed reflections [$I \geq 3\sigma(I)$]
$R_{\rm int} = 0.019$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = -26 \rightarrow 26$
3 standard reflections frequency: 60 min intensity decay: 1.0%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.047$
$S = 1.35$
2156 reflections
244 parameters
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.10$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl(1)	0.4140 (2)	0.0216 (2)	0.79492 (6)	6.89 (4)
Cl(2)	0.8169 (2)	0.0074 (2)	1.04446 (6)	6.89 (4)
Cl(3)	0.8290 (2)	−0.2155 (2)	0.95620 (7)	6.80 (4)
Cl(4)	0.4027 (2)	0.2437 (1)	0.88124 (7)	7.23 (4)
Cl(5)	−0.1543 (2)	−0.6194 (2)	0.90663 (8)	7.80 (4)
C(1)	0.5275 (6)	0.0192 (5)	0.8639 (2)	4.5 (1)
C(2)	0.5228 (6)	0.1172 (5)	0.9018 (2)	4.8 (1)
C(3)	0.6093 (6)	0.1127 (4)	0.9577 (2)	4.7 (1)
C(4)	0.7062 (6)	0.0102 (5)	0.9746 (2)	4.7 (1)
C(5)	0.7100 (6)	−0.0888 (5)	0.9360 (2)	4.6 (1)
C(6)	0.6170 (6)	−0.0830 (4)	0.8813 (2)	4.0 (1)
C(7)	0.2735 (6)	−0.3565 (4)	0.8858 (2)	3.8 (1)
C(8)	0.1300 (6)	−0.3581 (5)	0.8456 (2)	4.5 (1)
C(9)	−0.0010 (6)	−0.4389 (5)	0.8508 (2)	5.0 (1)
C(10)	0.0150 (6)	−0.5187 (5)	0.8978 (2)	4.8 (1)
C(11)	0.1525 (7)	−0.5179 (5)	0.9386 (2)	5.2 (1)
C(12)	0.2839 (7)	−0.4363 (5)	0.9333 (2)	5.0 (1)
O(1)	0.5964 (5)	0.2096 (3)	0.9930 (2)	6.8 (1)
C(13)	0.5198 (6)	−0.3550 (4)	0.7940 (2)	4.0 (1)
C(14)	0.5120 (6)	−0.4783 (4)	0.8032 (2)	3.8 (1)
C(15)	0.5284 (7)	−0.5591 (5)	0.7576 (2)	3.9 (1)
C(16)	0.5501 (7)	−0.5153 (5)	0.7016 (2)	5.7 (1)
C(17)	0.5580 (7)	−0.3937 (6)	0.6921 (2)	6.2 (1)
C(18)	0.5461 (7)	−0.3121 (5)	0.7380 (2)	5.3 (1)
O(2)	0.6242 (4)	−0.1785 (3)	0.8417 (1)	5.72 (7)
C(19)	0.5057 (6)	−0.2698 (4)	0.8427 (2)	4.2 (1)
N(1)	0.4070 (5)	−0.2684 (4)	0.8837 (2)	4.27 (9)

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

Cl(1)—C(1)	1.720 (5)	C(7)—N(1)	1.433 (5)
Cl(2)—C(4)	1.728 (4)	C(8)—C(9)	1.370 (6)
Cl(3)—C(5)	1.716 (5)	C(9)—C(10)	1.378 (6)
Cl(4)—C(2)	1.721 (5)	C(10)—C(11)	1.348 (6)
Cl(5)—C(10)	1.760 (4)	C(11)—C(12)	1.383 (6)
C(1)—C(2)	1.383 (6)	C(13)—C(14)	1.378 (6)
C(1)—C(6)	1.365 (6)	C(13)—C(18)	1.391 (6)
C(2)—C(3)	1.378 (6)	C(13)—C(19)	1.465 (5)
C(3)—C(4)	1.394 (7)	C(14)—C(15)	1.382 (6)
C(3)—O(1)	1.345 (5)	C(15)—C(16)	1.387 (7)
C(4)—C(5)	1.402 (6)	C(16)—C(17)	1.361 (7)
C(5)—C(6)	1.375 (6)	C(17)—C(18)	1.388 (6)
C(6)—O(2)	1.389 (5)	C(19)—O(2)	1.372 (5)
C(7)—C(8)	1.375 (6)	C(19)—N(1)	1.272 (5)
C(7)—C(12)	1.387 (6)		
Cl(1)—C(1)—C(2)	120.6 (4)	C(7)—C(8)—C(9)	121.3 (4)
Cl(1)—C(1)—C(6)	118.6 (3)	C(8)—C(9)—C(10)	118.5 (4)
C(2)—C(1)—C(6)	120.8 (4)	Cl(5)—C(10)—C(9)	119.1 (4)
Cl(4)—C(2)—C(1)	120.9 (4)	Cl(5)—C(10)—C(11)	119.1 (4)
Cl(4)—C(2)—C(3)	118.8 (4)	C(9)—C(10)—C(11)	122.0 (4)
C(1)—C(2)—C(3)	120.2 (5)	C(10)—C(11)—C(12)	119.7 (4)
C(2)—C(3)—C(4)	119.0 (4)	C(7)—C(12)—C(11)	119.7 (4)
C(2)—C(3)—O(1)	117.4 (5)	C(14)—C(13)—C(18)	119.2 (4)
C(4)—C(3)—O(1)	123.6 (5)	C(14)—C(13)—C(19)	120.6 (4)
Cl(2)—C(4)—C(3)	118.3 (4)	C(18)—C(13)—C(19)	120.1 (4)
Cl(2)—C(4)—C(5)	121.3 (4)	C(13)—C(14)—C(15)	120.8 (4)
C(3)—C(4)—C(5)	120.4 (4)	C(14)—C(15)—C(16)	119.6 (5)
Cl(3)—C(5)—C(4)	120.8 (4)	C(15)—C(16)—C(17)	120.0 (4)
Cl(3)—C(5)—C(6)	120.2 (4)	C(16)—C(17)—C(18)	120.8 (5)
C(4)—C(5)—C(6)	119.0 (4)	C(13)—C(18)—C(17)	119.6 (4)
C(1)—C(6)—C(5)	120.6 (4)	C(6)—O(2)—C(19)	118.2 (3)
C(1)—C(6)—O(2)	119.6 (4)	C(13)—C(19)—O(2)	110.7 (3)
C(5)—C(6)—O(2)	119.7 (4)	C(13)—C(19)—N(1)	131.3 (4)
C(8)—C(7)—C(12)	119.1 (4)	O(2)—C(19)—N(1)	118.0 (4)
C(8)—C(7)—N(1)	122.6 (4)	C(19)—N(1)—C(7)	121.3 (3)
C(12)—C(7)—N(1)	118.2 (4)		

The structure was solved by direct methods and difference Fourier syntheses. Refinement was by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms.

All calculations were performed on a PDP 11/44 computer with the *SDP* (Frenz, 1978) programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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