

Brooker's di-*tert*-butylmerocyanine

Norberto Masciocchi,* Patrizia Scuderi and Angelo Maspero

Dipartimento di Scienze Chimiche e Ambientali,
Università degli Studi dell'Insubria, via
Valleggio, 11, 22100 Como, ItalyCorrespondence e-mail:
norberto.masciocchi@uninsubria.it

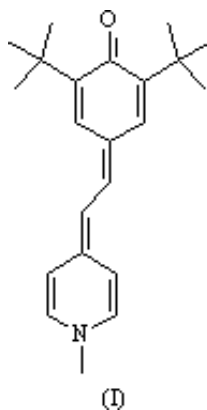
Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.071
 wR factor = 0.207
Data-to-parameter ratio = 15.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, 4-[(1-methyl-1,4-dihydropyridinylidene)ethylidene]-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one, $\text{C}_{22}\text{H}_{29}\text{NO}$, a green organic dye, possesses a quinone and not a zwitterionic structure in the solid state, thus differing significantly from the parent unsubstituted species.

Comment

4-[(1-Methyl-1,4-dihydropyridinylidene)ethylidene]-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one, (I), belongs to the class of so-called Brooker's merocyanines (Brooker *et al.*, 1951), which display a wide spectrum of solvatochromic properties (Reichardt, 1994; Kamlet *et al.*, 1981), depending on the ring substituents and on the relative importance of quinone or zwitterionic forms (the latter resulting in large hypsochromic shifts).



The molecular structure of the title compound closely resembles that of the parent 2,6-unsubstituted merocyanine (II) (De Ridder *et al.*, 1990), with the notable exception of the $\text{C}=\text{O}$ bond [1.253 (3) in (I), 1.304 (3) Å in (II)]. This shorter bond also imposes a wider spread of the $\text{C}-\text{C}$ bond distances in the cyclohexadienone ring [1.346 (4)–1.463 (4) Å], indicating a much more localized π system, with the $\text{C}=\text{O}$ bond of truly double character [1.222 (3) Å in benzoquinone at 173 K; van Bolhuis & Kiers, 1978]. Following this interpretation, the zwitterionic form proposed in a number of similar species (Morley *et al.*, 1997), and stabilized by hydrogen bonding in protic solvents, must be discarded in favour of a quinone form, responsible for the deep green (and not blue) colour. Interestingly, this species rapidly dissolves in acetone and gives a dark blue solution, in agreement with the experimental absorption energies, in a variety of solvents, for the title compound and other analogous species (Morley *et al.*, 1997; Da Silva *et al.*, 2002). In addition, the $\text{C8}-\text{C9}$ bond distance is significantly different [1.297 (4) *versus* 1.346 (4) Å], and can

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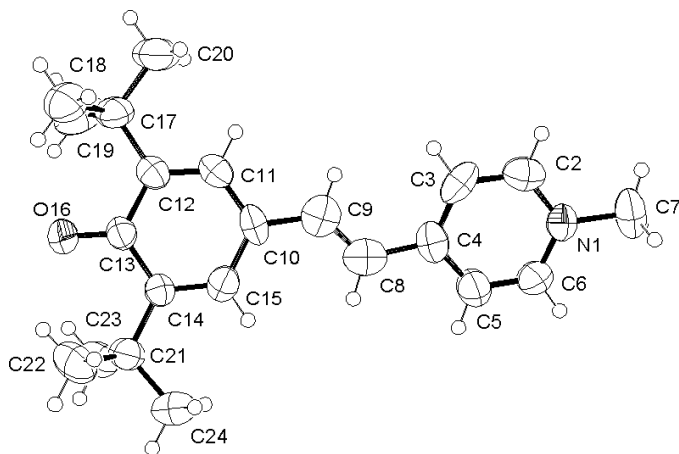


Figure 1

The molecular structure, with displacement ellipsoids drawn at the 50% probability level, of Brooker's di-*tert*-butyl-merocyanine. H atoms are depicted as circles of arbitrary size. Of the six disordered *N*-methyl H atoms, only one set of three is drawn here (one being eclipsed by the C atom).

be interpreted by the 'imperfect' location of the central C atoms. Indeed, due to a dynamic 'pedal-like' motion of the Ar–C=C–Ar fragment, these two atoms show unusually large displacement parameters (see Fig. 1), high residuals in the final difference Fourier map (see below) and, consequently, an anomalously short C=C distance. This experimental observation has been repeatedly observed in *trans*-stilbenes, diazobenzenes and other similar species, for which extensive X-ray characterizations at low temperatures and theoretical/computational studies have been published (Ogawa *et al.*, 1992; Galli *et al.*, 1999; Kwasniewski *et al.*, 2003).

The precision of the present crystal structure determination is indicated by the very limited spread [1.530 (4)–1.541 (4) Å] of chemically equivalent C–C bonds of the *tert*-butyl residues. In addition, the crystal packing is dictated by the presence of head-to-tail dimers, with intermolecular C···C distances slightly above 3.5 Å, generated by the $\bar{1}$ symmetry operation, and favoured by the antiparallel coupling of their high dipole moments (above 10 Debyes; Morley *et al.*, 1997).

Experimental

The title compound was prepared following the method described by Kay *et al.* (2001), using the properly disubstituted 4-hydroxybenzaldehyde and picolinium salt. More specifically, 1.00 g of 1,4-dimethylpyridinium iodide (4.25 mmol), 1.03 g of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (4.25 mmol) and 0.36 g of piperidine (4.25 mmol) were dissolved in 7 ml of anhydrous EtOH and refluxed for 22 h. After cooling to room temperature, a solid material formed, which was filtered off and washed four times with 15 ml of EtOH. This solid was then suspended in 25 ml of 0.2 M KOH solution, stirred and heated to 343 K. Upon cooling slowly to room temperature, the solution turned grey and a new solid could be recovered by filtration. Upon recrystallization from hot water, well shaped deep-green crystals (m.p. 548 K) were obtained.

Crystal data

C₂₂H₂₉NO
M_r = 323.46
 Monoclinic, *P*₂₁/*c*
a = 10.216 (2) Å
b = 15.445 (4) Å
c = 13.010 (6) Å
 β = 106.37 (2)°
V = 1969.6 (11) Å³
Z = 4

D_x = 1.091 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 9–16°
 μ = 0.07 mm⁻¹
T = 295 (2) K
 Prism, green
 0.20 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: none
 3631 measured reflections
 3429 independent reflections
 1756 reflections with *I* > 2σ(*I*)
R_{int} = 0.016

θ_{\max} = 24.9°
h = 0 → 12
k = 0 → 18
l = -15 → 14
 3 standard reflections
 frequency: 180 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.071
wR (*F*²) = 0.207
S = 1.02
 3429 reflections
 218 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 1.2544P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.68 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C4–C8	1.472 (4)	C13–C14	1.463 (4)
C8–C9	1.297 (4)	C14–C15	1.362 (4)
C9–C10	1.429 (4)	C17–C20	1.530 (4)
C10–C11	1.402 (4)	C17–C18	1.535 (5)
C10–C15	1.419 (4)	C17–C19	1.541 (4)
C11–C12	1.346 (4)	C21–C23	1.531 (4)
C12–C13	1.461 (4)	C21–C22	1.536 (4)
C13–O16	1.253 (3)	C21–C24	1.537 (4)
C5–C4–C8	119.6 (3)	C11–C10–C15	117.0 (2)
C3–C4–C8	125.8 (3)	C11–C10–C9	118.0 (3)
C9–C8–C4	124.4 (3)	O16–C13–C12	120.6 (2)
C8–C9–C10	129.4 (3)	O16–C13–C14	121.1 (2)
C4–C8–C9–C10	177.6 (3)		

Although most H atoms could be located in difference Fourier maps, they were eventually positioned geometrically (C–H = 0.93–0.96 Å) and refined using a riding model, with *U*_{iso}(H) = 1.2 or 1.5 times *U*_{eq}(C). The H atoms of the methyl group attached to N were refined in two conformations with 0.43 (4):0.57 (4) occupancy factors. The two largest residuals in the final difference Fourier map indicate the presence of a dynamic motion ('pedal'-like), typical for *trans*-stilbenes and similar species (see text). Some of the displacement parameters of the central C atoms, therefore, do not comply with the commonly employed Hirshfeld (1976) test. The unresolved disorder is probably responsible for the relatively high *R* factors.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local programs; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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