Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diethyl 4,5-bis(4-bromophenyl)-2-oxo-cyclopentadiene-1,3-dicarboxylate

David A. Grossie* and William A. Feld

Department of Chemistry, Wright State University, Dayton, Ohio 45435, USA

Correspondence e-mail:
david.grossie@wright.edu

Received 22 April 2004
Accepted 10 May 2004
Online 15 May 2004

The title compound, $C_{23}H_{18}Br_2O_5$, is one of a series of soluble precursors to electroluminescent conjugated polymers and helical structures. The geometries of the rings are within normal limits, as are those of the ethyl esters. There are few close contacts within the molecule, leading one to rationalize that the overall geometry arises from pure steric interactions without any attractive forces such as hydrogen bonding.

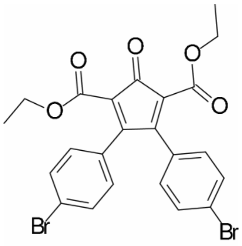
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.131
Data-to-parameter ratio = 18.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Cyclopentadienones produced by a condensation reaction are the building blocks used to produce many monomers used for light-emitting diodes. These cyclones can participate in Diels–Alder reactions with a large variety of internal and terminal acetylenes to generate a multitude of aromatic compounds.



(I)

The title compound, (I), reacts smoothly with norbornadiene or alkynes to generate aromatic terephthalic esters having phenyl and alkyl substituents. The terephthalic esters are a convenient substrate for the generation of a substituted 3,10-dibromo-5,8-dioxo-5,8-dihydroindeno[2,1-*c*]fluorene ring system by reaction with sulfuric acid (Lorge, 1998; Torres, 1999).

The cyclopentadienone and benzene rings are each planar, but are not coplanar. The benzene rings are twisted about the external bond to the five-membered ring by 44.7 (1)° for ring 1 (C31–C36) and 53.9 (1)° for ring 2 (C41–C46). The bond distances and angles around each atom are within accepted ranges.

A close contact of 3.398 (6) Å is noted between Br1 and Br1 in an adjacent molecule. This contact between bromine atoms lies roughly in the *b* direction within the unit cell. Examination of the displacement parameters of Br1 indicate a reduced thermal motion in this same direction. Many structures containing Br$\cdots$Br close contacts have been examined (Nyburg & Faerman, 1985). It is observed that an asymmetry in the contact radii for bromine occurs, ranging from 1.84 Å in the direction perpendicular to the C—Br bond, to 1.54 Å in the direction parallel to the C—Br bond. Furthermore, the

DOI: 10.1107/S1600536804011225

observed bromine radius could be fitted to a simple equation based on the Br···Br—C angle. Using the parameters found for bromine and the angle, 152.1 (1)°, a corrected radius of 1.704 Å is calculated. This value compares well with the Br···Br contact in the present structure.

Experimental

A solution of 4,4′-dibromobenzil (16 g, 0.0435 mol, 1 equivalent) and diethylacetonedicarboxylate (10.59 g, 0.052 mol, 1.21 equivalents) in ethanol (225 ml) was heated to reflux for 1 h and a sodium ethoxide solution (1.2 g Na^0 in 32.5 ml EtOH) was added slowly with stirring. The solution was held under reflux for 1 h, yielding a yellow precipitate. The mixture was cooled, and the precipitate was filtered off and air-dried overnight. The dry precipitate was slurried in 65 ml of acetic anhydride, and H_2SO_4 was added dropwise until the suspension turned translucent red and finally scarlet red. Water was added dropwise to decompose excess acetic anhydride, while maintaining the temperature of the solution below 353 K. The orange precipitate that formed was filtered off, air-dried and recrystallized from ligroine to yield 19.82 g (0.037 mol, 85%) of an orange solid, (I): m.p. 427–429 K (Torres, 1999).

Crystal data

$C_{23}H_{18}Br_2O_5$
M_r = 534.19
Monoclinic, $P2_1/n$
a = 10.7198 (8) Å
b = 7.7518 (5) Å
c = 26.447 (2) Å
β = 93.635 (1)°
V = 2193.3 (3) Å^3
Z = 4
D_x = 1.618 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5391 reflections
θ = 2.6–27.3°
μ = 3.73 mm^{-1}
T = 293 (2) K
Block, orange
0.7 × 0.6 × 0.6 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 1997–1999)
T_{min} = 0.097, T_{max} = 0.107
12 864 measured reflections
4998 independent reflections
3672 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.3°
h = −14 → 10
k = −9 → 9
l = −34 → 35

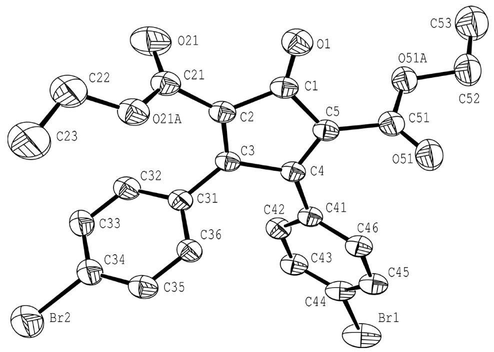


Figure 1
The molecular structure of (I), with all non-H atom displacement ellipsoids drawn at the 30% probability level.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.131
S = 1.02
4998 reflections
273 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0699P)^2 + 1.1998P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

H atoms were positioned geometrically and refined as riding, with methyl, methylene and aromatic C—H bond distances of 0.96, 0.97 and 0.93 Å, respectively. In all cases, $U_{iso}(H) = 1.3U_{iso}$(parent atom).

Data collection: *SMART* (Bruker, 1997–2000); cell refinement: *SAINT-Plus* (Bruker, 1997–1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *OSCAIL* (McArdle, 1995).

The authors acknowledge Allen Hunter for instrument time at Youngstown State University.

References

Bruker (1997–1999). *SAINT-Plus.* Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1997–2000). *SMART for WNT*/2000. Version 5.625. Bruker AXS Inc., Madison, Wisconsin, USA.
Lorge, E. A. (1998). MS thesis, Wright State University, Dayton, Ohio, USA.
McArdle, P. J. (1995). *J. Appl. Cryst.* **28**, 65–65.
Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* B**41**, 274–279.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Torres, M. D. (1999). MS thesis, Wright State University, Dayton, Ohio, USA.