Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,1′,8,8′-Tetramethoxy-10,10′-bianthrone

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Received 28 October 2004
Accepted 2 November 2004
Online 13 November 2004

The title compound, 1,1′,8,8′-tetramethoxy-9,9′-bianthracene-10,10′(9*H*,9′H)-dione, $C_{32}H_{26}O_6$, was obtained by the reduction of 1,8-dimethoxyanthraquinone with sodium borohydride and trifluoroacetic acid. In the anthrone dimers, the methoxy and carbonyl groups are attached to opposite sides of the anthracene rings. In the solid state, the molecule has a crystallographically imposed centre of symmetry located at the mid-point of the C—C bond linking the two anthracene systems.

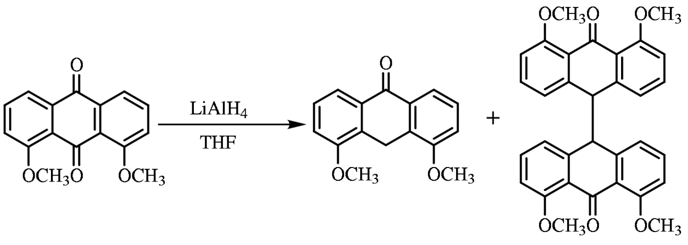
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.059
wR factor = 0.115
Data-to-parameter ratio = 13.8

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

Comment

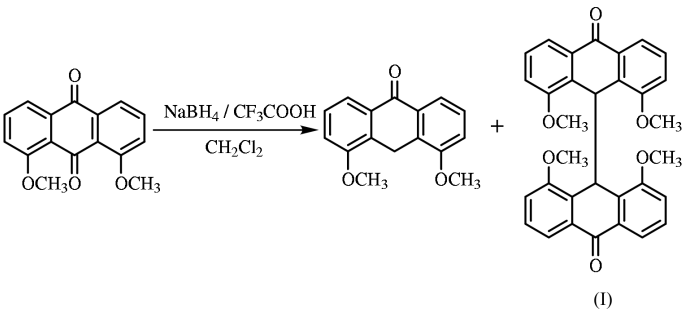
Anthracenone derivatives have interesting biological activities, which enhance their potency with regard to their use as drugs (Müller *et al.*, 1996, 1998, 2001; Prinz, Burgemeister & Wiegrebe, 1996; Prinz, Wiegrebe & Müller, 1996). Anthracenone derivatives are usually obtained by the reduction of anthraquinone derivatives. For example, 1,8-dimethoxy-10-anthrone is obtained by reduction with $LiAlH_4$/THF (THF is tetrahydrofuran) (Shyamasundar & Caluwe, 1981), $SnCl_2$/HCl (Müller & Leukel, 1994) or $Na_2S_2O_4$/DMF (DMF is dimethylformamide) (Prinz, Burgemeister & Wiegrebe, 1996; Prinz, Wiegrebe & Müller, 1996). In these procedures, only one carbonyl group was reduced to methylene. Furthermore, Shyamasundar & Caluwe (1981) reported that the reduction of 1,8-dimethoxyanthraquinone with $LiAlH_4$ led to the anthrone dimer (1), the minor reduction product, as well as 1,8-dimethoxy-10-anthrone as the major product. In this dimer, the methoxy and carbonyl groups are on the same side of the anthracene ring.



(1)

Recently, we also obtained a dimer of 1,8-dimethoxy-10-anthrone, during the reduction of 1,8-dimethoxyanthraquinone with sodium borohydride and trifluroacetic acid. The methoxy groups and the methine H atoms appeared at δ 3.64 and 5.85, respectively, in the ^{1}H NMR spectrum. Compared to Shyamasundar's dimer, (1), they were moved upfield by about δ 0.21 and 0.40. In order to explain these differences, the crystal structure of the title compound, (I), has been determined; it is presented here.

In the crystal structure, (I) has a centre of symmetry located at the mid-point of the C13—C13^i bond of length 1.594 (3) Å [symmetry code: (i) $-x$, $-y$, $2 - z$], which is longer than a normal single bond. The dimer adopts a less overlapped *transoid* conformation about the C13—C13^i bond (Fig. 1). Two methoxy and one carbonyl group are on different sides of the anthracene systems, corresponding to the dimer (I) rather than (1). The crystal packing (Fig. 2) is stabilized by van der Waals forces.



(I)

Experimental

The title anthrone dimer was prepared by reduction of 1,8-dimethoxyanthraquinone with sodium borohydride and trifluroacetic acid. 8–Dimethoxyanthraquinone was prepared in our laboratory and the other reagents were commercially available and were used without further purification. CF_3COOH (24 ml) was added dropwise with stirring to a solution of 1,8-dimethoxyanthraquinone (4.0 mmol) in 10 ml of anhydrous CH_2Cl_2. The mixture was then placed in an ice bath and $NaBH_4$ (0.8 g, 21 mmol) was added in portions. The resulting mixture was stirred for 30 h at room temperature. The reaction mixture was poured into 200 ml ice-water. The organic layer was extracted with CH_2Cl_2, dried over Na_2SO_4 and evaporated *in vacuo*. The crude product was recrystallizaed from toluene twice to give the main product 1,8-dimethoxy-10-anthrone (yield 83%). IR: 1657 cm^{-1} (ν C═O). MS (EI): *m*/*e* = 254 (M^+, 100%). ^{1}H NMR (300 Mz, $CDCl_3$): δ 7.99 (*d*, *J* = 7.90 Hz, 2H, ArH in 4,5-moiety), 7.43 (*dd*, *J*1 = 7.95, *J*2 = 8.00 Hz, 2H, ArH in 2, 7-moiety), 7.13 (*d*, *J* = 8.00 Hz, 2H, ArH in 3, 6-moiety), 4.10 (*s*, 2H, ArH2 in 9-moiety), 4.00 (*s*, 6H, 2 × $ArOCH_3$). Analysis calculated for $C_{16}H_{14}O_3$: C 75.57, H 5.55%; found: C 75.46, H 5.66%. The combined filtrates were concentrated until cloudiness appeared. Toluene was added and the clear solution was brought to room temperature. The white solid was filtered off and recrystallized once again from toluene to give white needle crystals of (I) (yield 4.5%, m.p. > 573 K). Single crystals suitable for X-ray crystallographic analysis were prepared by slow evaporation of a solution of (I) in chloroform–ethanol (2:1 *v*/*v*). MS (EI): *m*/*e* = 254 ($M^+/2 + 1$, 100%); ^{1}H NMR(300Mz, $CDCl_3$): δ 7.42 (*d*, *J* = 7.74 Hz, 4H, ArH in 4,4′,5,5′-moiety), 7.31 (*dd*, *J*1 = 7.94, *J*2 = 7.85 Hz, 4H, ArH in 3,3′,6,6′-moiety), 6.88 (*d*, *J* = 8.00 Hz, 4H, ArH in 2,2′,7,7′-moiety), 5.85 (*s*, 2H, ArH in 9,9′-moiety), 3.64 (*s*, 12H, 4 × $ArOCH_3$). Analysis calculated for $C_{32}H_{26}O_6$: C 75.88, H 5.17%; found: C 75.95, H 5.22%.

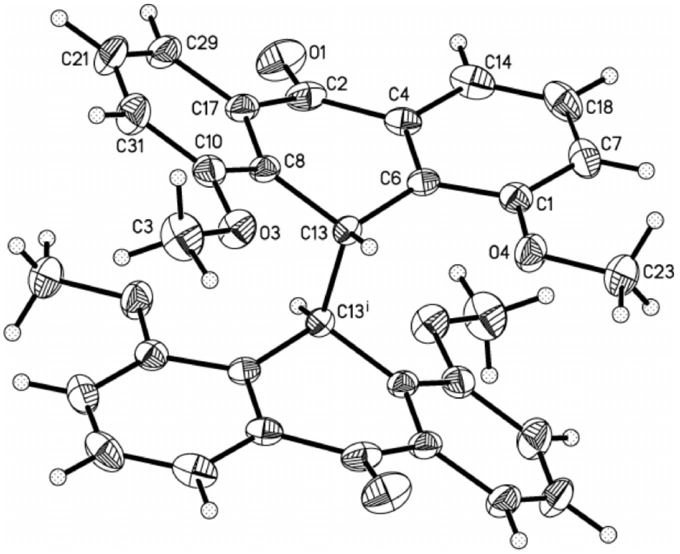


Figure 1
View of (I) with 30% probability displacement ellipsoids [symmetry code: (i) $-x$, $-y$, $2 - z$].

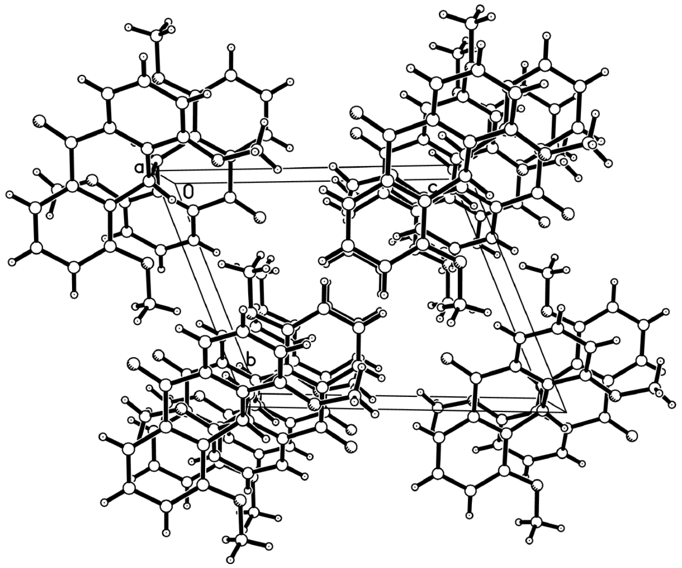


Figure 2
The crystal packing of (I), viewed down the *a* axis.

Crystal data

$C_{32}H_{26}O_6$
M_r = 506.53
Triclinic, $P\overline{1}$
a = 7.585 (2) Å
b = 8.443 (2) Å
c = 10.631 (3) Å
α = 67.801 (4)°
β = 74.187 (4)°
γ = 85.328 (5)°
V = 606.3 (3) Å^3
Z = 1
D_x = 1.387 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 523 reflections
θ = 2.6–25.9°
μ = 0.10 mm^{-1}
T = 293 (2) K
Block, white
0.32 × 0.26 × 0.24 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.97, T_{max} = 0.98
4784 measured reflections
2392 independent reflections
1381 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 26.0°
$h = -8 \rightarrow 9$
$k = -9 \rightarrow 10$
$l = -11 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.115$
$S = 1.01$
2392 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.038$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.027 (4)

All H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.96 Å, and included in the refinement in the riding-model approximation, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (grant No. 90101018) and Science Foundation of JiangSu Province in China (grant No. BK2004085).

References

Bruker (2000). *SMART* (Version 5.625), *SAINT* (Version 6.01), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.

Müller, K., Altmann, R. & Prinz, H. (1998). *Eur. J. Med. Chem.* **33**, 209–214.

Müller, K., Breu, K. & Reindl, H. (2001). *Eur. J. Med. Chem.* **36**, 179–184.

Müller, K., Huang, H—S. & Wiegrebe, W. (1996). *J. Med. Chem.* **39**, 3132–3128.

Müller, K., Leukel, P., Ziereis K. & Gawlik I. (1994). *J. Med. Chem.* **37**, 1660–1669.

Prinz, H., Burgemeister, T., Wiegrebe, W. (1996). *J. Org. Chem.* **61**, 2857–2860.

Prinz, H., Wiegrebe, W. & Müller, K. (1996). *J. Org. Chem.* **61**, 2853–2856.

Shyamasundar, N. & Caluwe, P. (1981). *J. Org. Chem.* **46**, 1552–1557.