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Key indicators

Single-crystal X-ray study
 $T = 120\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.055
 wR factor = 0.143
Data-to-parameter ratio = 14.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Diethyl 9,10-endo-ethano-9,10-dihydro-
anthracene-11,11-dicarboxylate

The title compound, $\text{C}_{22}\text{H}_{22}\text{O}_4$, possesses normal geometrical parameters and the dihedral angle between the two benzene ring planes is $57.62(5)^\circ$. The crystal packing is controlled by van der Waals forces and a possible $\text{C}-\text{H}\cdots\text{O}$ interaction, the latter resulting in a supramolecular $C(6)$ motif.

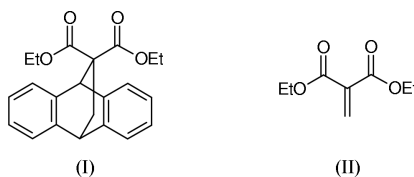
Received 14 May 2004

Accepted 20 May 2004

Online 29 May 2004

Comment

The title compound, (I) (Fig. 1), was created as an intermediate in the synthesis of 2-methylene malonic acid diethyl ester, (II). The alkene produced in the absence of anthracene is very unstable and polymerizes easily. The presence of the anthracene acts to trap the monomer in a Diels–Alder reaction and purification of (I) prior to thermolysis allows the generation of (II) (by a retro-Diels–Alder reaction) in a much more stable form. The presence of excess maleic anhydride in this reaction ensures that the released anthracene is consumed by the formation of an anthracene-maleic anhydride adduct and is not free to regenerate (I). Thus, this type of reaction may be useful in the trapping of alkenes and allow for easier purification.



The geometrical parameters for (I) are broadly similar to those of related 9,10-bridged anthracene derivatives (Table 1) (Gable *et al.*, 1996; Karolak-Wojciechowska *et al.*, 1998; Burrows *et al.*, 1999). The two benzene rings in (I) (atoms C2–C7 and C9–C14) are both essentially planar (r.m.s. deviations from the least-squares planes are 0.010 and 0.001 Å, respectively). The dihedral angle between these rings is $57.62(5)^\circ$, which is typical for these 9,10-bridged anthracene systems, e.g. the corresponding dihedral angle in 11,12-bis(*N,N*-dimethylaminomethyl)-9,10-dihydro-9,10-ethanoanthracene (Karolak-Wojciechowska *et al.*, 1998) is $58.8(2)^\circ$. The three six-membered rings of the bicyclic core of (I) (C1/C2/C7/C8/C9/C14, C1/C2/C7/C8/C15/C16 and C1/C14/C9/C8/C15/C16; see Fig. 1) are all forced into boat forms. The ester substituents show no unusual features.

The only significant intermolecular interaction in (I), as identified in a *PLATON* (Spek, 2003) analysis of the structure, is a $\text{C8}-\text{H8}\cdots\text{O3}^{\text{i}}$ bond (Table 2). This bridgehead H8 atom attached to an sp^3 -hybridized C atom may be slightly activated due to ring strain (Desiraju & Steiner, 1999). This connectivity results in $C(6)$ chains (Bernstein *et al.*, 1995), generated by *n*-

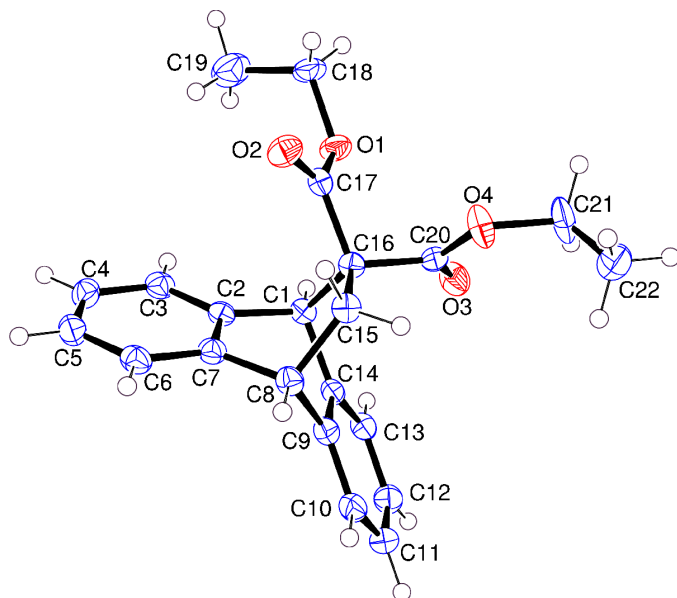


Figure 1
View of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius.

glide symmetry (Fig. 2). Otherwise, the crystal packing is controlled by van der Waals forces.

Experimental

A round-bottomed flask was fitted with a still head and condenser and diethyl malonate (9.70 g, 9.2 ml, 61 mmol), anthracene (12.00 g, 67 mmol), paraformaldehyde (3.64 g, 0.12 mol), copper(II) acetate monohydrate (0.60 g, 3.0 mmol), acetic acid (50 ml) and xylene (50 ml) were quickly added. The reaction mixture was heated at 383 K for 15 h and a clear dark-green solution resulted. The temperature was increased in order to distil off the acetic acid, then the reaction mixture was cooled to room temperature and filtered under suction. The filtrate was retained and the xylene evaporated on a rotary evaporator to yield a green oil which was left to crystallize. Purification was carried out by recrystallization from hot hexane. Filtration and washing with ice-cold hexane (25 ml) resulted in the pure anthracene adduct (I) (14.72 g, 69%) as colourless plates [m.p. 404.5–405 K; literature (De Keyser *et al.*, 1988) 403–404 K from EtOH]; R_f (hexane–propan-2-ol 50:1) 0.13; ν_{\max} (KBr disc)/ cm^{-1} : 2974 (C–H), 1732 (C=O), 1460–1446 (aromatic C=C) and 757 (4 adjacent Ar-H); δH (250 MHz; CDCl_3): 1.15 (6H, *t*, $J = 7.0$ Hz, $2 \times \text{CH}_3$), 2.47 [2H, *d*, $J = 2.4$ Hz, $(\text{EtO}_2\text{C})_2\text{CCH}_2$], 3.95–4.09 (4H, *m*, $2 \times$

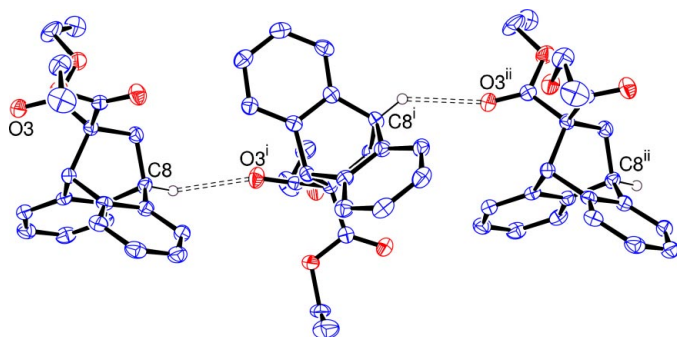


Figure 2
Detail of a chain of molecules of (I) linked by C–H...O interactions. [Symmetry codes: (i) as in Table 2; (ii) $x + 1, y, z + 1$.]

OCH₂), 4.33 (1H, poorly resolved *t*, $J = 2.4$ Hz, Ar₂CHCH₂), 4.97 [1H, *s*, Ar₂CHC(CO₂Et)₂] and 7.07–7.33 (8H, *m*, Ar-H); δC (CDCl_3): 14.0, 36.4, 43.9, 49.6, 60.0, 61.7, 123.3, 125.7, [De Keyser *et al.* (1988) give 125.68 and 125.74], 126.4, 139.8, 144.0 and 170.2.

Crystal data

$\text{C}_{22}\text{H}_{22}\text{O}_4$
 $M_r = 350.40$
Monoclinic, $P2_1/n$
 $a = 9.2424$ (2) Å
 $b = 16.5210$ (5) Å
 $c = 11.9154$ (4) Å
 $\beta = 98.631$ (2)°
 $V = 1798.80$ (9) Å³
 $Z = 4$

$D_x = 1.294$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 21 98 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 0.09$ mm⁻¹
 $T = 120$ (2) K
Plate, colourless
 $0.28 \times 0.20 \times 0.03$ mm

Data collection

Enraf–Nonius KappaCCD diffractometer
 ω and φ scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.976$, $T_{\max} = 0.999$
21 237 measured reflections

3538 independent reflections
2750 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.120$
 $\theta_{\max} = 26.0^\circ$
 $h = -11 \rightarrow 11$
 $k = -20 \rightarrow 20$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.143$
 $S = 1.06$
3538 reflections
238 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.8446P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ e Å⁻³
Extinction correction: SHELXL97
Extinction coefficient: 0.012 (3)

Table 1

Selected geometrical parameters (Å, °).

C1–C16	1.576 (3)	C15–C16	1.559 (3)
C8–C15	1.550 (3)		
C20–C16–C17–O2	−131.2 (2)	C17–C16–C20–O3	−109.9 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
C8–H8 ⁱ ...O3 ⁱ	1.00	2.56	3.380 (2)	139

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

All H atoms were geometrically placed in idealized locations and refined as riding on their carrier C atoms with C–H distances set to 0.95, 0.98, 0.99 and 1.00 Å for aromatic, sp^2 , terminal sp^3 and bridgehead sp^3 hybrid C atoms, respectively. The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ was applied as appropriate.

Data collection: COLLECT (Nonius, 1998); cell refinement: COLLECT and DENZO (Otwinowski & Minor, 1997); data reduction: COLLECT and DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

We thank the EPSRC UK National Crystallography Service (University of Southampton) for the data collection.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Burrows, L., Masnovi, J. & Baker, R. J. (1999). *Acta Cryst.* **C55**, 236–239.
- De Keyser, J.-L., De Cock, C. J. C., Poupaert, J. H. & Dumont, P. (1988). *J. Org. Chem.* **53**, 4859–4862.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*. Oxford: IUCr/OUP.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gable, R. W., Qureshi, A. & Schiesser, C. H. (1996). *Acta Cryst.* **C52**, 674–675.
- Karolak-Wojciechowska, J., Trzeźwińska, H. B., Alibert-Franco, S., Santelli-Rouvier, C. & Barbe, J. (1998). *J. Chem. Crystallogr.* **28**, 905–911.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.