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Diethyl 9,10-dihydro-9,10-ethano-
anthracene-11,12-*trans*-dicarboxylate

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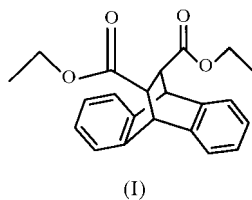
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The title compound, $C_{22}H_{22}O_4$, is the product of the Diels-Alder reaction of anthracene with fumaric acid diethyl ester. The molecular C_2 symmetry is nearly fulfilled in the crystal. Only the terminal torsion angles about the O—CH₂ groups show significant differences.

Comment

The title compound, (I), is the product of a [4+2]-cycloaddition reaction of anthracene and fumaric acid diethyl ester. The X-ray structure analysis was carried out in order to confirm the identity of this compound.



The title compound consists of a 9,10-dihydroanthracene moiety with an ethano bridge connecting the C atoms in positions 9 and 10. This bridge effects a narrowing of the angle between the two aromatic rings in unsubstituted 9,10-dihydroanthracene from 144.7 (Herbstein *et al.*, 1986) and 144.5° (Reboul *et al.*, 1987) to 117.22 (4)° in (I). If the bridge is not substituted, as in 9,10-ethano-9,10-dihydroanthracene (Burrows *et al.*, 1999), the angle between the two aromatic rings is only reduced to 124.7°. However, bond lengths and angles are similar for all these four mentioned structures. Both carbonic acid diethyl ester groups show the same conformation: the methylene groups C53 and C63 are *cis* to the carbonyl O atoms O51 and O61, respectively. This feature can also be observed for nearly all structures containing this fragment retrieved from the Cambridge Structural Database (Allen & Kennard, 1993). The only molecule in which the torsion angle is definitely in a *trans* conformation is ethyl acetate, which was

found as a solvent in several crystal structures. The title compound is nearly C_2 -symmetrical. A least-squares fit of all atoms with its 180° rotated image about an axis running through the centre of the C15—C16 bond yields an r.m.s.d. of 0.118 Å. The only significant difference between the two halves is between the torsion angles C51—O52—C53—C54 171.0 (2)° and C61—O62—C63—C64 153.8 (2)°.

Experimental

The title compound was synthesized according to Hünig *et al.* (1979). Anthracene (20.0 mmol) and fumaric acid diethyl ester (20.0 mmol) were dissolved in dry methylene chloride (60 ml). The solution was cooled in an ice bath and dry AlCl₃ (20.0 mmol) was added. Then the solution was stirred at room temperature for about 2 h. The product was precipitated at 273 K and filtered. The residue was a white crystalline solid. Recrystallization from diethyl ether yielded crystals suitable for X-ray diffraction.

Crystal data

$C_{22}H_{22}O_4$
 $M_r = 350.40$
 Monoclinic, $P2_1/n$
 $a = 7.8786$ (7) Å
 $b = 18.417$ (1) Å
 $c = 12.758$ (1) Å
 $\beta = 96.971$ (5)°
 $V = 1837.5$ (2) Å³
 $Z = 4$

$D_x = 1.267$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 510 reflections
 $\theta = 1-20^\circ$
 $\mu = 0.086$ mm⁻¹
 $T = 173$ (2) K
 Block, colourless
 $0.70 \times 0.50 \times 0.50$ mm

Data collection

Siemens CCD three-circle diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.942$, $T_{\max} = 0.958$
 34 998 measured reflections
 4656 independent reflections
 4052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 29.62^\circ$
 $h = -9 \rightarrow 10$
 $k = -22 \rightarrow 25$
 $l = -17 \rightarrow 17$
 123 standard reflections
 frequency: 1200 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.138$
 $S = 1.029$
 4656 reflections
 236 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.9045P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0147 (16)

The data collection nominally covered a sphere of reciprocal space, by a combination of eight sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω . The crystal-to-detector distance was 5.5 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. All H atoms were initially located by difference Fourier synthesis. Subsequently, their positions were idealized and constrained to ride on their parent atoms with C—H(aromatic) = 0.95, C—H(methyl) = 0.98, C—H(secondary) = 0.99 or C—H(tertiary) = 1.00 Å, and fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{aromatic}})$ or $U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$].

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

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