

Dimethyl 9,10-anthracenedicarboxylate: a centrosymmetric *transoid* molecule

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In the crystal structure of the title compound, $C_{18}H_{14}O_4$, there are two independent molecules, both of which are exactly centrosymmetric and therefore have a *transoid* arrangement of the ester substituents. The planes of these are inclined at 63.90 (4) and 61.02 (5)° to the anthracene central ring in the two molecules because of steric interactions, preventing electronic delocalization. The observed conformation is in agreement with molecular-modelling calculations for the isolated molecule, indicating no major influence from crystal-packing forces.

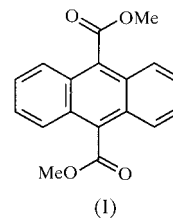
Comment

The conflicting demands of electronic conjugation and steric interference are well known in many types of organic molecules, particularly aromatic compounds with appropriate unsaturated substituents. A classic case is that of biphenyl, which appears to adopt an essentially planar conformation in the crystalline solid state (Trotter, 1961; Charbonneau & Delugeard, 1976, 1977), but is twisted by *ca* 45° about the central C—C bond in the gas phase (Almenningen *et al.*, 1985; Bastiansen & Samdal, 1985); the steric interaction of *ortho*-H atoms is unfavourable for a coplanar arrangement of the two rings, but this is advantageous for delocalization between the rings, and the balance between the two factors is tipped in favour of planarity in the solid state by intermolecular interactions. A carboxyl substituent on a benzene ring, as in carboxylic acids, esters and other derivatives, tends to lie approximately in the plane of the ring, provided there are no adverse steric interactions with other substituents. This can be illustrated by a search of the Cambridge Structural Database (Allen & Kennard, 1993) for 1,4-dicarboxyl-substituted benzene with no other substituents, for example; these are terephthalic acid itself and its salts, esters, metal complexes and other molecules incorporating the terephthalate unit. Of the 55 structures reported, only three have the carboxyl group

rotated more than 20° out of the ring plane, and a large majority of dihedral angles are under 10°. By contrast, higher polycarboxylates involving substituent groups on adjacent ring C atoms, such as derivatives of pyromellitic acid with a 1,2,4,5-tetrasubstituent pattern, cannot adopt a fully planar configuration and so have large dihedral angles.

In the case of 9,10-disubstituted anthracenes with unsaturated substituents such that a double bond $X=Y$ might be conjugated to the central ring, steric interference may occur between outer ring H atoms and groups attached to X and Y and also the atom Y itself. Port *et al.* (1997) have reported the synthesis and structural characterization of anthracenes substituted at both the 9 and 10 positions with either tertiary butyl ketone or tertiary butyl imine groups. For these compounds, the steric interactions are so great that there is highly restricted rotation about the substituent bonds to the anthracene nucleus, and distinct *cisoid* and *transoid* isomers can be isolated. The crystal structures of the two isomeric imines were determined, and both have the substituents almost perpendicular to the central ring plane.

In the course of studies on 9,10-difunctionalized anthracene derivatives we prepared the title compound, (I), by a modification of the method of Duerr *et al.* (1988) and obtained suitable crystals for X-ray diffraction analysis. We have determined the structure for comparison with other anthracenes having unsaturated substituents in the 9 and 10 positions.



The structure contains two symmetry-independent molecules, each lying on a crystallographic inversion centre, so that the asymmetric unit is two half-molecules. They are shown in Fig. 1 and have essentially identical geometry. Intermolecular interactions are of standard van der Waals type only, with no significant face-to-face stacking of aromatic rings. Since the molecules are strictly centrosymmetric, they have a *transoid* conformation of the two substituents. The mean planes of the esters (excluding H atoms) lie at dihedral angles of 63.90 (4) and 61.02 (5)° to the anthracene nucleus for the two molecules. In keeping with the steric interactions and lack of conjugation between the anthracene nucleus and the substituents, the C9—C13 and C9A—C13A bonds are relatively long for bonds between Csp^2 atoms.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for molecules with two $X=Y$ double bonds (with any substituents allowed) attached to the 9 and 10 positions of an otherwise unsubstituted anthracene molecule produces just seven structures, including the two isomers of the diimine reported by Port *et al.* (1997). The substituents range from nitro (Trotter, 1959) to an imidazolyl hydrazone in two different salts with anticancer properties (Bates *et al.*,

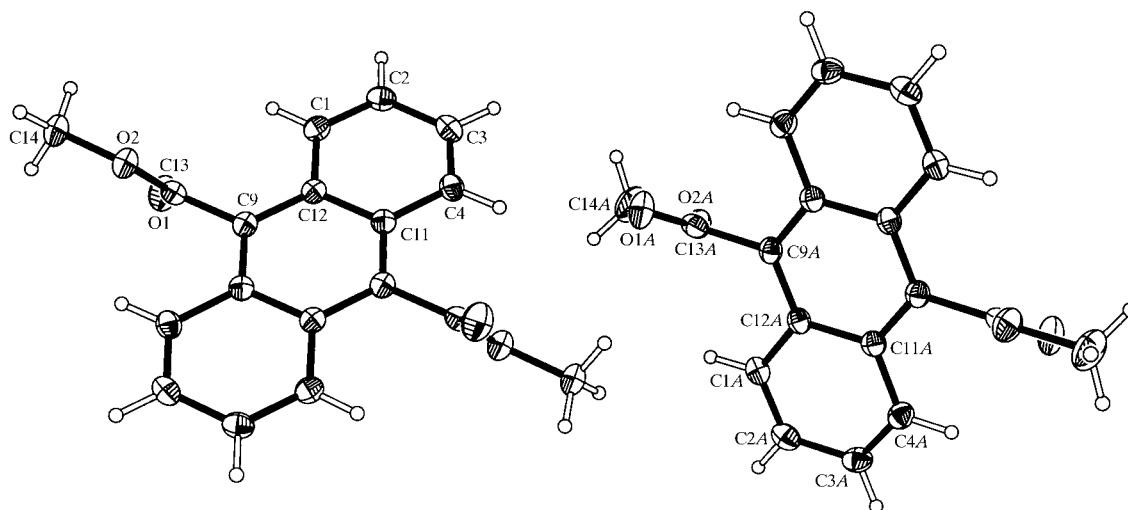


Figure 1

The molecular structure with atom labels and 50% probability displacement ellipsoids for non-H atoms.

1986; Pierpont & Lang, 1986) and include two ketones (Harlow *et al.*, 1975; Sundell & Becker, 1994), but there are no previously reported esters. With the exception of the *cisoid* isomer of the diimine, all these molecules have crystallographic inversion symmetry (including two independent molecules in each of three cases) and are *transoid*. Most of the dihedral angles between the central aromatic ring and the substituents lie in the range 40–90°, indicating a strong steric interference which prevents effective conjugation. The one exception is a dihedral angle of only 4.6° for one of the two independent molecules in a hydrazone (Bates *et al.*, 1986), for which the other molecule has a dihedral angle of 41.3°. The other salt of this same cationic hydrazone (Pierpont & Lang, 1986) has a dihedral angle of 48.7°, and these values are significantly smaller than the dihedral angles for the remaining compounds. The hydrazone, for which $X = \text{CH}$ and $Y = \text{NR}$ with only one substituent directed away from the anthracene nucleus, clearly suffers much less steric interaction than the other molecules, particularly so in comparison with the ketones and the imines, for all of which the dihedral angles exceed 75°. The dinitro compound has a value of 61.8° for the dihedral angle, in keeping with the intermediate steric demands in this case, and a very similar result is found in the ester reported here, for which the substituents have comparable steric requirements.

The question arises whether the barrier to rotation about the substituent bonds is sufficiently high for a *cisoid* form of the title compound to be isolated as a separate isomer from the *transoid* form. Molecular modelling, with augmented *MM3* parameters and an optimized map generated by searching the dihedral angle of the ester group at 15° intervals (Oxford Molecular, 1999), gave four possible low-energy conformations, two of which were *cisoid* and two *transoid*. The energies of these forms were similar, and the activation energy for interconversion between *cisoid* and *transoid* forms was around 9 kcal mol⁻¹ (1 cal = 4.184 J). This is substantially less than the 25 kcal mol⁻¹ value observed for the analogous di-*tert*-butyl-

imines (Port *et al.*, 1997). No evidence could be obtained, however, for the presence of a second isomer in the ¹H NMR spectra in the temperature range 193 to 373 K in toluene solution. Further experiments are being carried out in order to investigate the existence of the *cisoid* form of this molecule. Subsequent global energy minimization of the lowest energy conformation of the *transoid* form gave dihedral angles of 65.9 and 64.4° for the two ester groups, which are in very good agreement with the observed conformation in the crystalline state. The dihedral angles of the second low-energy conformer are 64.4 and 67.2°.

Experimental

A stirred mixture of 9,10-dibromoanthracene (2.0 g, 5.96 mmol) in anhydrous diethyl ether (20 ml) was cooled in an ice bath, then *n*-butyllithium (9.76 ml of a 1.6 M solution in hexane, 15.6 mmol) was added dropwise from a syringe. The mixture was allowed to warm to room temperature and stirred for 30 min. After cooling again in ice, dry carbon dioxide (from evaporation of solid through a silica gel trap) was passed over the mixture for 1 h. Water (10 ml) and diethyl ether (10 ml) were then added, the aqueous phase separated, washed with two more portions of diethyl ether (2 ml), acidified with 1 M sulfuric acid (pH 2.0), and the resulting yellow product filtered off and dried *in vacuo*. Thionyl chloride (100 ml) was added to the dried product (1.26 g) and the resulting mixture heated at reflux overnight. The thionyl chloride was then removed *in vacuo*. Anhydrous methanol (50 ml) was added, and the solution was heated at reflux for 2.5 h and then evaporated to dryness. Recrystallization by slow evaporation of dichloromethane/petrol (333–353 K) yielded 0.92 g (52% overall yield) of golden plates. Subsequent recrystallization of a small sample under the same conditions gave golden needles that were used in this study; m.p. 441–443 K (literature 448–449 K from MeOH; Duerr *et al.*, 1988); ¹H NMR (CDCl₃, p.p.m.) δ 7.98 (*dd*, 4H, $J = 6.8, 3.4$ Hz, Ar-H), 7.54 (*dd*, 4H, $J = 6.8, 3.4$ Hz, Ar-H), 4.15 (*s*, 6H, OCH₃); ¹³C NMR (CDCl₃, p.p.m.) δ 169.7 (C=O), 130.7 (C9, C10), 127.7 (Ar-C), 127.0 (Ar-CH), 125.4 (Ar-CH), 52.9 (MeO).

Crystal data

C₁₈H₁₄O₄
M_r = 294.29
 Monoclinic, *P*2₁/*c*
a = 18.4434 (14) Å
b = 6.8590 (5) Å
c = 11.5334 (9) Å
 β = 107.488 (2)°
V = 1391.58 (18) Å³
Z = 4

D_x = 1.405 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 7819 reflections
 θ = 2.31–28.57°
 μ = 0.099 mm⁻¹
T = 160 (2) K
 Plate, colourless
 0.80 × 0.50 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
 ω rotation with narrow frames
 11 472 measured reflections
 3322 independent reflections
 2719 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.017
 θ_{\max} = 28.57°
h = -23 → 24
k = -9 → 8
l = -15 → 15

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.038
wR (*F*²) = 0.105
S = 1.064
 3322 reflections
 201 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.2247P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1–C13	1.2022 (14)	O1A–C13A	1.1922 (14)
O2–C13	1.3273 (14)	O2A–C13A	1.3243 (15)
O2–C14	1.4491 (14)	O2A–C14A	1.4439 (15)
C9–C13	1.5129 (15)	C9A–C13A	1.5182 (16)
C13–O2–C14	115.32 (9)	C13A–O2A–C14A	114.79 (10)
O1–C13–O2	124.48 (11)	O1A–C13A–O2A	125.62 (12)
O1–C13–C9	123.60 (10)	O1A–C13A–C9A	124.09 (11)
O2–C13–C9	111.91 (9)	O2A–C13A–C9A	110.29 (9)
C14–O2–C13–C9	179.14 (9)		
C11 ⁱ –C9–C13–O1	-116.06 (13)		
C12–C9–C13–O1	62.36 (15)		
C11 ⁱ –C9–C13–O2	65.06 (13)		
C12–C9–C13–O2	-116.52 (11)		
C14A–O2A–C13A–C9A	179.24 (10)		
C12A–C9A–C13A–O1A	119.48 (13)		
C11A ⁱⁱ –C9A–C13A–O1A	-61.19 (16)		
C12A–C9A–C13A–O2A	-61.07 (13)		
C11A ⁱⁱ –C9A–C13A–O2A	118.26 (11)		

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) -*x*, 1 - *y*, -*z*.

H atoms were placed geometrically and refined with a riding model (including free rotation about C–C bonds), and with *U*_{iso} constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1083). Services for accessing these data are described at the back of the journal.

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