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A diaryl-terminated hexa-1,5-diyne-3,4-dione

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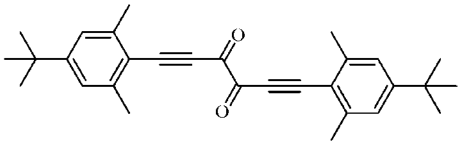
The structure of bis(4-*tert*-butyl-2,6-dimethylphenyl)hexa-1,5-diyne-3,4-dione, $C_{30}H_{34}O_2$, has been determined, revealing an extended *s-trans* conformation of the dione and the two ynone moieties, which are shielded by the flanking methyl substituents. The structural parameters and the packing arrangement suggest little electronic delocalization between the two ynone moieties.

Comment

The title compound, (I), is a newly synthesized member of the diacetylenic 1,2-diones, a class of compounds first introduced in 1996 (Faust & Weber, 1996; Faust *et al.*, 1997). The two typifying interconnected ynone moieties of this molecular structure give rise to a rich chemistry which we have explored to form, *inter alia*, metal-chelating diazabutadienes (Faust, Göbelt & Weber, 1999; Faust, Göbelt, Weber *et al.*, 1999), alkyne-substituted nitrogen-heterocyclic carbenes (Faust & Göbelt, 2000) and acetylenic phthalocyanines (Faust, 2001). Despite these successful developments, two questions remain about the electronic aspects of these compounds. Firstly, the kinetic stability of dialkynyldiones appears to rely largely on the size of the terminal alkyne substituents. Whereas bulky triisopropylsilyl groups lend excellent stability to the hexadiynedione core, smaller terminal substituents, such as alkyls or the trimethylsilyl group, are insufficient to protect the reactive ynone system from nucleophilic attack (Faust *et al.*, 1997). Similarly, aryl termini shield the reactive core of the molecule most effectively when, as in the case discussed here, they possess sizeable 2,6-substituents flanking the alkyne subunit. The second question concerns the effective conjugation path of the hexa-1,5-diyne-3,4-dione framework. We have speculated that, similar to the related 2,3-dialkynyl-1,4-diazabutadienes (Faust, Göbelt, Weber *et al.*, 1999), a valid description of dialkynyldiones is that of two interconnected but largely electronically independent bis(ynone) units, rather than that of a species fully delocalized along the hexadiynedione core. The present solid-state study is the first on this class of compounds and was undertaken to shed some light on these matters.



(I)

The title compound, (I), with the atomic numbering, is shown in Fig. 1. The molecule crystallizes in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit. Inspection of Fig. 1 reveals an extended conformation of the molecule, with a formal *s-trans* geometry [torsion angle O2—C4—C3—O1 175.2 (2) °] around the 1,2-dione subunit. The maximum deviation of the atoms from the plane through C2/C3/C4/C5/O1/O2 is only 0.062 (1) Å for atom C5. The plane through C1/C2/C3/C7/C8/C12/O1 forms an angle of only 4.2 (1)° with that of the dione substructure, indicating that the C7-benzene ring is almost perfectly coplanar with the dione unit. On the other hand, the plane through C4/C5/C6/C19/C20/C24 (involving the C19-benzene ring) is twisted by about 20.3 (1)° from the plane of the dione moiety.

In terms of π electronic delocalization, it appears that, in the crystal structure, the electronic interaction between one benzene group and the ynone portion of the molecule is maximized, whereas that of the other is slightly diminished. The distance between the two carbonyl atoms C3—C4 is 1.535 (2) Å (Table 1), suggesting a rather long Csp^2—Csp^2

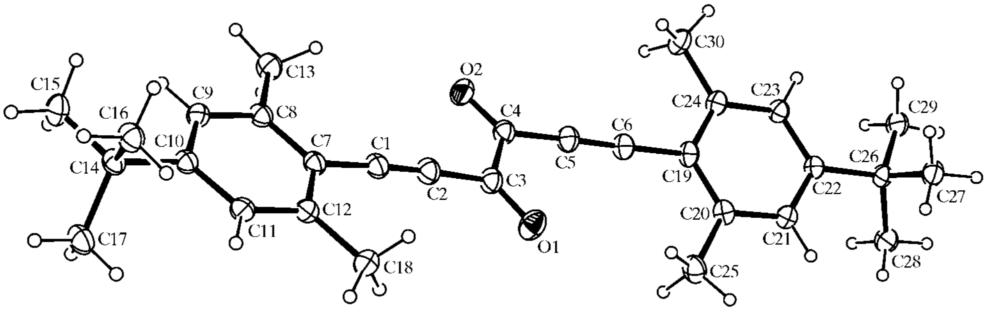


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

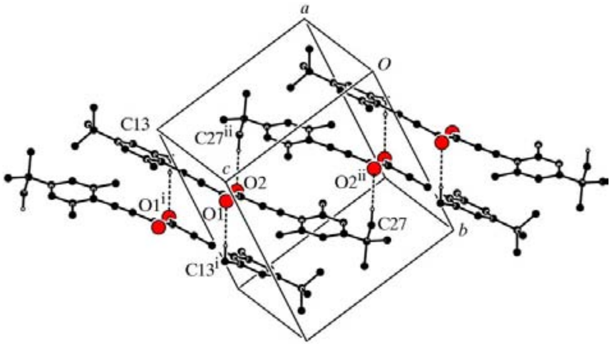


Figure 2
The packing of (I), revealing the closest distances between the O atoms and the methyl groups of neighbouring molecules (dashed lines); see Table 2 for details.

single bond through which little electron density is transmitted. While most other structural parameters within this part of the molecule are within the normal range (Allen *et al.*, 1987), the C—C—C angles around the carbonyl C atoms [*i.e.* C2—C3—C4 = 116.7 (1)° and C3—C4—C5 = 114.5 (1)°] are significantly compressed.

The methyl groups in the 2,6-positions on the aryl rings protrude above and below the C1≡C2 and C5≡C6 triple bonds, a structural feature that helps to explain the increased stability of this system towards nucleophilic attack, particularly in solution, where there is free rotation around the C7—C1 and C6—C19 single bonds. There are no close intramolecular contacts between the methyl H atoms and the carbonyl O atoms.

An inspection of the packing arrangement (Fig. 2) of compound (I) in the crystal reveals that the *tert*-butyl groups of one molecule reside in the space above the dione subunits of adjacent molecules. In conjunction with the findings above, this might indicate that the planarity of the dione substructure is dictated by the space requirements of the bulky alkyl group rather than by intramolecular electronic interactions such as π delocalization. The crystal packing forces are enhanced by very weak intermolecular hydrogen bonds between methyl H atoms and carbonyl O atoms. The relevant distances are depicted as dashed lines in Fig. 2, with details given in Table 2. In this way, chains of centrosymmetric rings develop along [101]. The alkyl substitution of the aryl rings prevents intermolecular π–π stacking interactions.

Experimental

Compound (I) was synthesized from 4-*tert*-butyl-2,6-dimethylphenylacetylene and oxalyl chloride, following the procedure outlined in Faust *et al.* (1997) [m.p. 437 K (decomposition)]. IR (neat, ν, cm^{-1}): 2953, 2176, 1664, 1107; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.05 (4H, *s*, CH), 2.47 (12H, *s*, CH$_3$), 1.28 (18H, *s*, CH$_3$); ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 173.31, 155.28, 143.79, 124.46, 116.32, 93.74, 80.99, 34.93, 30.98, 21.24; APCI–MS: 427 (33) $[M + H]^+$; 399 (70) $[M - CO + H]^+$; 213 (100) $[M/2]^+$. Single crystals of (I) suitable for X-ray diffraction studies were obtained by slow evaporation from acetonitrile.

Crystal data

$C_{30}H_{34}O_2$
M_r = 426.57
Triclinic, $P\overline{1}$
a = 9.3933 (11) Å
b = 11.4531 (14) Å
c = 11.9823 (13) Å
α = 93.289 (9)°
β = 105.303 (9)°
γ = 93.674 (10)°
V = 1237.1 (3) Å^3
Z = 2
D_x = 1.145 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 11 904 reflections
θ = 1.8–25.6°
μ = 0.07 mm^{-1}
T = 213 (2) K
Block, yellow
0.58 × 0.32 × 0.31 mm

Data collection

Stoe IPDS-2 diffractometer
Rotation scans
Absorption correction: integration (*X-RED*; Stoe, 2004)
$T_{\min}$ = 0.974, $T_{\max}$ = 0.991
15 963 measured reflections
4296 independent reflections

3130 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.055
$\theta_{\max}$ = 25.0°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.107
S = 1.00
4296 reflections
300 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.023 (4)

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.203 (2)	C4—C5	1.437 (2)
C1—C7	1.4321 (19)	C5—C6	1.205 (2)
C2—C3	1.440 (2)	C6—C19	1.4330 (19)
C3—O1	1.2139 (18)	C8—C13	1.502 (2)
C3—C4	1.535 (2)	C11—C12	1.384 (2)
C4—O2	1.2139 (18)		
C1—C2—C3	174.50 (17)	C5—C4—C3	114.51 (13)
C2—C3—C4	116.65 (13)	C6—C5—C4	173.22 (16)
O1—C3—C4—O2	175.22 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13A···O1$^{\rm i}$	0.97	2.59	3.545 (2)	168
C27—H27A···O2$^{\rm ii}$	0.97	2.59	3.558 (2)	173

Symmetry codes: (i) $-x + 2, -y + 1, -z + 2$; (ii) $-x + 1, -y + 1, -z + 1$.

H atoms were placed in geometric positions and treated as riding, with C—H distances in the range 0.94–0.97 Å and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1824). Services for accessing these data are described at the back of the journal.

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