Boeré, René T.

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(E)-1,2-Bis(3-bromo-4-methylphenyl)-ethene

Department of Chemistry and Biochemistry

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In the structure of the title compound, C_{16}H_{14}Br_{2}, the central C=C bond length is 1.329 (4) Å and the two benzene rings are approximately coplanar with the double bond, with twist angles of 7.5 (2) and 13.6 (2)°.

Related literature

For related literature, see: Daik et al. (1998); Harada & Ogawa et al. (2004); Ogawa et al. (1992); Mallory et al. (2001).

Experimental

Crystal data

C_{16}H_{14}Br_{2}

M_r = 366.09
Monoclinic, P2_1/c

a = 6.3301 (4) Å

b = 7.6499 (5) Å

V = 28.164 (2) Å³

\beta = 91.208 (1)°

V = 1363.55 (16) Å³

Z = 4

Mo Kα radiation

μ = 5.92 mm⁻¹

T = 173 (2) K

0.27 × 0.19 × 0.10 mm

14025 measured reflections

2793 independent reflections

165 parameters

H-atom parameters constrained

Δρ_{max} = 0.42 e Å⁻³

Δρ_{min} = −0.32 e Å⁻³

Support provided by Dr Peter Dibble and the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. The diffractometer was purchased with the help of NSERC and the University of Lethbridge.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2061).

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(E)-1,2-Bis(3-bromo-4-methylphenyl)ethene

René T. Boeré and Steven J. Robbins

S1. Comment
The title compound, (I) (Fig. 1), was prepared by a Ti catalyzed McMurray coupling (Mallory et al., 2001) with 99% E selectivity. The almost-planar molecules pack (Fig. 2) in slipped stacks with T-contacts typical for aromatic molecules. The only other isomeric stilbene for which a structure has been reported is Z-1,2-bis-(4-bromophenyl)-1,2-dimethyl-ethene (Daik et al., 1998) for which C=C is 1.330 (10) and 1.344 (10)Å (for two independent molecules in an asymmetric unit). Unlike in I, the phenyl rings in this compound are twisted almost orthogonal to the double bond, perhaps because of steric interactions between methyl and phenyl groups. More structurally comparable alkenes include E-1,2-bis-(2,4-dimethylphenyl)ethene and E-1,2-bis-(2,4,5-trimethylphenyl)ethene (Ogawa et al., 1992) for which C=C are 1.320 (4) and 1.327 (3) Å, respectively. A detailed study of geometric distortions in trans-stilbene has recently been published (Harada & Ogawa, 2004).

S2. Experimental
At 273 K under N2, 0.18 ml (1.6 mmol) of TiCl4 was stirred with 0.18 g (2.8 mmol) Zn dust in 25 ml of dry THF. To this mixture was added 0.25 g (1.3 mmol) of 3-bromo-4-methylbenzaldehyde and refluxed for 4 h before being quenched with 25 ml of 1.0 M HCl. After extracting with hexanes the organic phase was washed with brine solution and dried over MgSO4. Removal of solvent resulted in a white powder that was recrystallized from ethyl acetate to give 0.11 g (yield = 58%) of the desired product as colorless crystals.

S3. Refinement
The H-atoms were included in the refinements at geometrically idealized positions with C—H distances 0.95 and 0.98 Å for non-methyl and methyl type H-atoms, respectively; Uiso values were 1.2Ueq of the carrier atom or 1.5Ueq for the non-methyl and methyl groups, respectively.
Figure 1
A view of (I) plotted with displacement ellipsoids at 50% probability level.

Figure 2
Unit-cell contents of (I) showing the herringbone arrangement of slipped-stacks with T-contacts between registers.

(E)-1,2-Bis(3-bromo-4-methylphenyl)ethene

Crystal data
C_{16}H_{14}Br_{2}  
Mr = 366.09
Monoclinic, P2_{1}/c
Hall symbol: -P2ybc
a = 6.3301 (4) Å
b = 7.6499 (5) Å
c = 28.164 (2) Å
β = 91.208 (1)°
V = 1363.55 (16) Å^{3}
Z = 4
F(000) = 720
D_{x} = 1.783 Mg m^{-3}
Melting point: 424.75 K
Mo Kα radiation, λ = 0.71073 Å
μ = 5.92 mm^{-1}
T = 173 K
Prism, colourless
0.27 × 0.19 × 0.10 mm

Data collection
Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube, Bruker D8
Graphite monochromator
θ and ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2004)
T_{min} = 0.303, T_{max} = 0.578
14025 measured reflections
2793 independent reflections
2393 reflections with I > 2σ(I)
R_{int} = 0.027
θ_{max} = 26.4°, θ_{min} = 2.8°
h = −7→7
k = −9→9
l = −35→35
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R(F^2) = 0.025$

$wR(F^2) = 0.054$

$S = 1.09$

2793 reflections

165 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 1.6865P]$

$\Delta/\sigma_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.43 \text{ e Å}^{-3}$

$\Delta\rho_{\text{min}} = -0.32 \text{ e Å}^{-3}$

Special details

Geometry. All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

Refinement. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{Å}^2$)

| Atom | $x$     | $y$     | $z$     | $U_{eq}$/$U_{eq}$ |
|------|---------|---------|---------|-------------------|
| Br1  | 0.08255 (4) | 0.93057 (4) | 0.56250 (9) | 0.02689 (8) |
| C1   | 0.0145 (4)  | 0.8529 (3)  | 0.62456 (8) | 0.0197 (5)  |
| C2   | −0.1806 (4) | 0.7739 (3)  | 0.63183 (9) | 0.0217 (5)  |
| C3   | −0.2158 (4) | 0.7151 (3)  | 0.67779 (10)| 0.0241 (6)  |
| H3   | −0.3476     | 0.6620     | 0.6844    | 0.029*      |
| C4   | −0.0673 (4) | 0.7309 (3)  | 0.71400 (9)| 0.0237 (6)  |
| H4   | −0.0972     | 0.6867     | 0.7446    | 0.028*      |
| C5   | 0.1280 (4)  | 0.8119 (3)  | 0.70600 (9)| 0.0213 (6)  |
| C6   | 0.1650 (4)  | 0.8749 (3)  | 0.66049 (9)| 0.0212 (5)  |
| H6   | 0.2939      | 0.9332     | 0.6541    | 0.025*      |
| C7   | 0.2912 (4)  | 0.8315 (4)  | 0.74343 (9)| 0.0241 (6)  |
| H7   | 0.4101      | 0.9015     | 0.7361    | 0.029*      |
| C8   | −0.3452 (4) | 0.7506 (4)  | 0.59307 (10)| 0.0282 (6) |
| H8A  | −0.2872     | 0.6792     | 0.5676    | 0.034*      |
| H8B  | −0.3865     | 0.8653     | 0.5804    | 0.034*      |
| H8C  | −0.4693     | 0.6922     | 0.6060    | 0.034*      |
| Br2  | 0.44176 (4) | 0.73105 (4)| 0.971236 (9)| 0.02871 (8) |
| C11  | 0.5297 (4)  | 0.7870 (3)  | 0.90906 (9)| 0.0205 (5)  |
| C12  | 0.7254 (4)  | 0.8675 (3)  | 0.90274 (9)| 0.0218 (5)  |
| C13  | 0.7768 (4)  | 0.9044 (3)  | 0.85612 (10)| 0.0243 (6) |
| H13  | 0.9102      | 0.9558     | 0.8501    | 0.029*      |
| C14  | 0.6420 (4)  | 0.8695 (4)  | 0.81816 (9)| 0.0253 (6)  |
| H14  | 0.6834      | 0.8991     | 0.7869    | 0.030*      |
| C15  | 0.4454 (4)  | 0.7913 (3)  | 0.82503 (9)| 0.0218 (6)  |
| C16  | 0.3931 (4)  | 0.7476 (3)  | 0.87155 (9)| 0.0224 (6)  |
H16 0.2629 0.6906 0.8774 0.027*
C17 0.2894 (4) 0.7613 (4) 0.78658 (9) 0.0250 (6)
H17 0.1761 0.6842 0.7932 0.030*
C18 0.8708 (4) 0.9153 (4) 0.94351 (10) 0.0279 (6)
H18A 0.8014 1.0011 0.9638 0.033*
H18B 1.0011 0.9656 0.9313 0.033*
H18C 0.9047 0.8104 0.9621 0.033*

Atomic displacement parameters (Å²)

|     | \(U^{11}\)  | \(U^{22}\)  | \(U^{33}\)  | \(U^{12}\)  | \(U^{13}\)  | \(U^{23}\)  |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| Br1 | 0.02994 (15)| 0.03138 (16)| 0.01930 (14)| −0.00196 (12)| −0.00088 (10)| 0.00574 (11)|
| C1  | 0.0243 (14) | 0.0192 (13) | 0.0157 (12) | 0.0034 (11)  | 0.0018 (10)  | 0.0006 (10)  |
| C2  | 0.0207 (13) | 0.0217 (14) | 0.0226 (13) | 0.0025 (11)  | −0.0021 (10) | −0.0016 (11)|
| C3  | 0.0214 (13) | 0.0219 (14) | 0.0291 (15) | 0.0000 (11)  | 0.0031 (11)  | 0.0012 (11)  |
| C4  | 0.0295 (15) | 0.0221 (14) | 0.0196 (13) | 0.0031 (11)  | 0.0033 (11)  | −0.0001 (11)|
| C5  | 0.0252 (14) | 0.0196 (13) | 0.0190 (13) | 0.0025 (11)  | 0.0001 (11)  | −0.0042 (10)|
| C6  | 0.0193 (13) | 0.0224 (14) | 0.0218 (13) | −0.0019 (11) | 0.0014 (10)  | −0.0017 (11)|
| C7  | 0.0253 (14) | 0.0256 (15) | 0.0213 (14) | 0.0010 (11)  | 0.0001 (11)  | −0.0028 (11)|
| C8  | 0.0247 (14) | 0.0314 (16) | 0.0283 (15) | −0.0022 (12) | −0.0052 (11) | −0.0001 (12)|
| Br2 | 0.03120 (16)| 0.03709 (17)| 0.01781 (14)| −0.00261 (12)| −0.00030 (11)| 0.00279 (12)|
| C11 | 0.0259 (14) | 0.0184 (13) | 0.0172 (13) | 0.0044 (11)  | 0.0003 (10)  | 0.0014 (10)|
| C12 | 0.0221 (13) | 0.0169 (13) | 0.0262 (14) | 0.0042 (10)  | −0.0029 (11) | −0.0014 (11)|
| C13 | 0.0192 (13) | 0.0218 (14) | 0.0321 (15) | 0.0008 (11)  | 0.0027 (11)  | 0.0016 (11)|
| C14 | 0.0298 (15) | 0.0249 (14) | 0.0213 (14) | 0.0026 (12)  | 0.0030 (11)  | 0.0018 (11)|
| C15 | 0.0251 (14) | 0.0185 (13) | 0.0217 (13) | 0.0028 (11)  | −0.0017 (11) | −0.0011 (10)|
| C16 | 0.0216 (13) | 0.0216 (14) | 0.0240 (14) | −0.0008 (11) | −0.0008 (10) | 0.0009 (11)|
| C17 | 0.0287 (15) | 0.0243 (14) | 0.0218 (14) | −0.0022 (12) | −0.0013 (11) | −0.0023 (11)|
| C18 | 0.0272 (15) | 0.0248 (15) | 0.0314 (15) | −0.0020 (12) | −0.0052 (12) | −0.0019 (12)|

Geometric parameters (Å, °)

|        |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|--------|
| Br1—Cl | 1.904 (2) | Br2—C11 | 1.898 (3) |
| C1—C6  | 1.386 (3) | C11—C16 | 1.385 (4) |
| C1—C2  | 1.393 (4) | C11—C12 | 1.398 (4) |
| C2—C3  | 1.393 (4) | C12—C13 | 1.389 (4) |
| C2—C8  | 1.504 (4) | C12—C18 | 1.502 (4) |
| C3—C4  | 1.378 (4) | C13—C14 | 1.380 (4) |
| C3—H3  | 0.9500   | C13—H13 | 0.9500   |
| C4—C5  | 1.405 (4) | C14—C15 | 1.398 (4) |
| C4—H4  | 0.9500   | C14—H14 | 0.9500   |
| C5—C6  | 1.394 (4) | C15—C16 | 1.399 (4) |
| C5—C7  | 1.468 (4) | C15—C17 | 1.468 (4) |
| C6—H6  | 0.9500   | C16—H16 | 0.9500   |
| C7—C17 | 1.329 (4) | C17—H17 | 0.9500   |
| C7—H7  | 0.9500   | C18—H18A | 0.9800 |
| C8—H8A | 0.9800   | C18—H18B | 0.9800 |
| C8—H8B | 0.9800   | C18—H18C | 0.9800 |
C8—H8C 0.9800

| Bond | Angle 1  | Angle 2  | Angle 3  |
|------|---------|---------|---------|
| C6—C1—C2 | 122.9 (2) | C16—C11—C12 | 122.7 (2) |
| C6—C1—Br1 | 117.82 (19) | C16—C11—Br2 | 117.7 (2) |
| C2—C1—Br1 | 119.25 (19) | C12—C11—Br2 | 119.67 (19) |
| C3—C2—C1 | 115.9 (2) | C13—C12—C11 | 115.9 (2) |
| C3—C2—C8 | 120.9 (2) | C13—C12—C18 | 121.4 (2) |
| C1—C2—C8 | 123.2 (2) | C11—C12—C18 | 122.7 (2) |
| C4—C3—C2 | 122.6 (3) | C14—C13—C12 | 122.7 (3) |
| C4—C3—H3 | 118.7 | C14—C13—H13 | 118.7 |
| C2—C3—H3 | 118.7 | C12—C13—H13 | 118.7 |
| C3—C4—C5 | 120.6 (2) | C13—C14—C15 | 120.9 (2) |
| C3—C4—H4 | 119.7 | C13—C14—H14 | 119.6 |
| C5—C4—H4 | 119.7 | C15—C14—H14 | 119.6 |
| C6—C5—C4 | 117.7 (2) | C14—C15—C16 | 117.5 (2) |
| C6—C5—C7 | 119.7 (2) | C14—C15—C17 | 123.5 (2) |
| C4—C5—C7 | 122.6 (2) | C16—C15—C17 | 119.0 (2) |
| C1—C6—C5 | 120.2 (2) | C11—C16—C15 | 120.4 (2) |
| C1—C6—H6 | 119.9 | C11—C16—H16 | 119.8 |
| C5—C6—H6 | 119.9 | C15—C16—H16 | 119.8 |
| C17—C7—C5 | 126.6 (3) | C7—C17—C15 | 126.4 (3) |
| C17—C7—H7 | 116.7 | C7—C17—H17 | 116.8 |
| C5—C7—H7 | 116.7 | C15—C17—H17 | 116.8 |
| C2—C8—H8A | 109.5 | C12—C18—H18A | 109.5 |
| C2—C8—H8B | 109.5 | C12—C18—H18B | 109.5 |
| H8A—C8—H8B | 109.5 | H18A—C18—H18B | 109.5 |
| C2—C8—H8C | 109.5 | C12—C18—H18C | 109.5 |
| H8A—C8—H8C | 109.5 | H18A—C18—H18C | 109.5 |
| H8B—C8—H8C | 109.5 | H18B—C18—H18C | 109.5 |
| Br2—C11—C12—C18 | −1.0 (3) | C6—C5—C7—C17 | −171.7 (3) |
| Br1—C1—C2—C8 | −1.7 (4) | C16—C15—C17—C7 | 162.7 (3) |
| C4—C5—C7—C17 | 8.2 (4) | C5—C7—C17—C15 | −175.4 (2) |
| C14—C15—C17—C7 | −14.1 (4) | | |