

## ORGANIC COMPOUNDS

*Acta Cryst.* (1999). C55, 2078–2080**(E)-3,4-Di-*tert*-butylhex-3-ene-2,5-dione**OLIVER KLEIN,<sup>a</sup> INA DIX,<sup>a</sup> HENNING HOPF<sup>a</sup> AND PETER G. JONES<sup>b\*</sup><sup>a</sup>*Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and* <sup>b</sup>*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

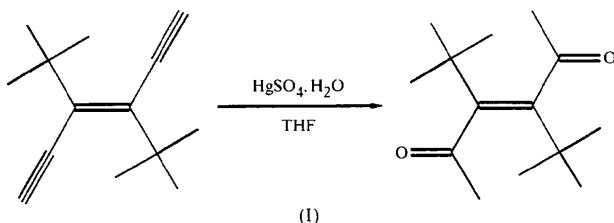
(Received 19 March 1999; accepted 7 October 1999)

**Abstract**

The title compound, C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>, is a member of the family of sterically crowded olefins that show unusual geometries. The molecule displays crystallographic inversion symmetry. The central double bond is slightly elongated [1.344 (3) Å]. In order to avoid steric repulsion, the C—C(*tert*-butyl) single bonds are markedly longer than in non-crowded ethylenes. Furthermore, the acetyl function is rotated out of the plane defined by the central double bond by 78.71 (6)°. The crystal packing shows C—H···O hydrogen bonds forming a honeycomb-like pattern.

**Comment**

Several years ago we reported an attempt to prepare tetra-*tert*-butylethene from its tetraacetyl precursor (Dannheim *et al.*, 1987). Although this approach was unsuccessful, we still believe that acetyl groups could, in principle, serve as precursor substituents for *tert*-butyl groups in highly hindered olefins, and we have therefore sought other methyl ketones that could lead to the elusive hydrocarbon. A derivative of interest in this context is (*E*)-3,4-di-*tert*-butylhex-3-ene-2,5-dione, (I), which we have synthesized recently (Klein, 1997) and whose structure we report in the present communication.



Steric repulsion in double-bond systems with bulky substituents can be diminished by elongation of bonds and rotation of substituents out of the double-bond

plane. The title compound, which displays crystallographic inversion symmetry, shows both of the above-mentioned features. The central double bond [C3=C3<sup>i</sup> = 1.344 (3) Å; symmetry code: (i) 1 - x, 1 - y, 1 - z] is slightly elongated compared with standard values for tetrasubstituted ethylenes without bulky groups (1.331 Å; Allen *et al.*, 1987). The C—C(*tert*-butyl) single bond of 1.555 (2) Å is distinctly stretched in comparison with substituted Csp<sup>2</sup>—Csp<sup>2</sup> single bonds (1.522 Å; Allen *et al.*, 1987). Similar bond elongations are observed in ethylene compounds bearing two *tert*-butyl groups on the central C=C double bond; 1.574 (2) and 1.568 (3) Å in (*E*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (ROLBID; Gano *et al.*, 1997) and 1.532 (2) Å in (*E*)-2,2,5,5-tetramethyl-3,4-bis[4-(tribromomethyl)phenyl]hex-3-ene (TEJNOL; Gano *et al.*, 1996).

Additionally, the C=C—*t*Bu angle (C3<sup>i</sup>—C3—C4) is widened to 127.1 (2)°. The same effect can be recognized in the bulkily substituted ethylenes mentioned above, where the corresponding angles are 127.0 (2) and 126.6 (2)° (Gano *et al.*, 1997), and 128.9 (8)° (Gano *et al.*, 1996).

The Csp<sup>2</sup>—Csp<sup>2</sup> single bond C—C(O) is significantly longer [C2—C3 1.513 (2) Å] than in unconjugated ketones (1.484 Å; Allen *et al.*, 1987), but lies within the range of comparable compounds such as tetrabenzoyl-ethylene [1.52 (1)–1.53 (2) Å; TBOYEV; Cannon *et al.*, 1978] and tetraacetylene [1.506 (2) Å; TACETY; Cannon *et al.*, 1978]. This bond length indicates that there is no double-bond character. Consequently, there is no conjugation between the ethylenic double bond and the ketone functions. This is reflected in a twisting of the acetyl function C1—C2—O (mean deviation 0.011 Å) by 78.71 (6)° out of the plane (mean deviation 0.001 Å) defined by the central C=C double bond and its attached atoms.

The dominant feature of the crystal packing is the presence of non-conventional hydrogen bonds. The hydrogen-bond system is built up from only one crystallographically independent hydrogen bond of type C—H···O between an acetyl methyl group and a carbonyl function. The H1C atom is involved in a hydrogen bond to O<sup>ii</sup> [C1···O 3.449 (3) Å; symmetry code (ii)  $\frac{3}{2} - x, y - \frac{1}{2}, z$ ], forming chains parallel to (010) [graph set C(4)]. The characteristic distances of this hydrogen bond agree with the criteria of Desiraju (1996). A further chain can be recognized parallel to (100) [graph set C(7)]. Because of the connection of the two chains, a honeycomb-like pattern within layers perpendicular to the z axis is formed, which can be described by the graph set R<sub>4</sub><sup>4</sup>(22) (Fig. 2). The layer sequence is an ABAB system with layer B antiparallel to layer A. The centres of the six-membered rings are related to each other by the vector **b**/2.

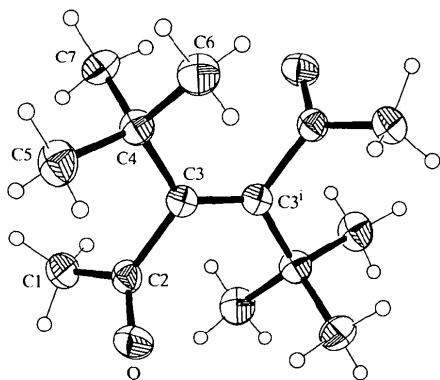


Fig. 1. The molecule of compound (I) in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]

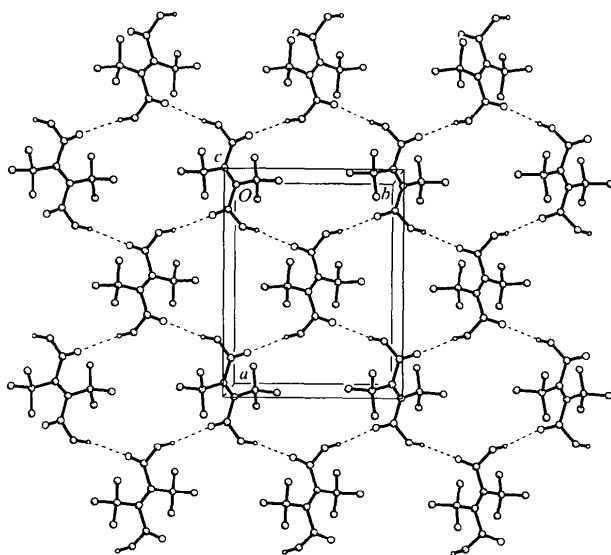


Fig. 2. The crystal packing of compound (I). Only the H atoms involved in hydrogen bonding are shown.

The open packing as shown in Fig. 2 is reflected in a low crystal density of  $1.108 \text{ Mg m}^{-3}$ .

## Experimental

$\text{HgSO}_4$  (90 mg, 0.3 mmol) and concentrated sulfuric acid (0.2 ml) were diluted with water (10 ml). The reaction mixture was heated to 333 K and a solution of (*E*)-3,4-di-*tert*-butylhex-3-ene-1,5-diyne (90 mg, 0.48 mmol; Hopf & Horn, 1994) in tetrahydrofuran (5 ml) was added. The reaction solution was stirred for 3 h at 333 K. After cooling to ambient temperature, water (10 ml) was added and the aqueous layer extracted with diethyl ether. The organic layers were combined, washed with  $\text{NaHCO}_3$  and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by column chromatography ( $\text{SiO}_2$ ; pentane–diethyl ether, 10:1). The product was obtained in 40% yield (43 mg, m.p. 371 K). Slow evaporation of a pentane solution gave colourless crystals.

## Crystal data

$\text{C}_{14}\text{H}_{24}\text{O}_2$   
 $M_r = 224.33$   
 Orthorhombic  
*Pbca*  
 $a = 12.412(2) \text{ \AA}$   
 $b = 9.680(2) \text{ \AA}$   
 $c = 11.191(2) \text{ \AA}$   
 $V = 1344.6(4) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.108 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 48 reflections  
 $\theta = 10.0\text{--}11.5^\circ$   
 $\mu = 0.072 \text{ mm}^{-1}$   
 $T = 143(2) \text{ K}$   
 Tablet  
 $0.60 \times 0.50 \times 0.15 \text{ mm}$   
 Colourless

## Data collection

Stoe Stadi-4 diffractometer  
 $\omega/\theta$  scans  
 Absorption correction: none  
 1428 measured reflections  
 1188 independent reflections  
 952 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 25.04^\circ$   
 $h = -14 \rightarrow 2$   
 $k = 0 \rightarrow 11$   
 $l = -13 \rightarrow 0$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.134$   
 $S = 1.058$   
 1188 reflections  
 77 parameters  
 H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 0.4841P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters and hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ )

C2—C3	1.513(2)	C3—C4	1.555(2)	
C3—C3'	1.344(3)			
C3'—C3—C4	127.1(2)			
D—H...A	D—H	H...A	D...A	D—H...A
C1—H1C...O <sup>ii</sup>	0.98	2.51	3.449(3)	162

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, z$ .

Data collection: *DIF4* (Stoe & Cie, 1992a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL97*.

This work forms part of the PhD thesis of OK. We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1331). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Cannon, J. R., Patrick, V. A., Raston, L. & White, A. H. (1978). *Aust. J. Chem.* **31**, 1265–1283.
- Dannheim, J., Grahn, W., Hopf, H. & Parrodi, C. (1987). *Chem. Ber.* **120**, 871–872.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Gano, J. E., Kirschbaum, K. & Sekher, P. (1996). *Acta Cryst.* **C52**, 2334–2337.
- Gano, J. E., Kluwe, C., Kirschbaum, K., Pinkerton, A. A., Sekher, P., Skrzypczak-Jankun, E., Subramaniam, G. & Lenoir, D. (1997). *Acta Cryst.* **C53**, 1723–1725.
- Hopf, H. & Horn, C. (1994). *Chem. Ber.* **127**, 1781–1796.
- Klein, O. (1997). Diploma thesis, Technical University of Braunschweig, Germany.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoe & Cie (1992a). *DIF4. Diffractometer Control Software*. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1992b). *REDU4. Data Reduction Software*. Stoe & Cie, Darmstadt, Germany.

*Acta Cryst.* (1999). **C55**, 2080–2084

## Polysulfonylamines. CXXI.† Three *N,N*-disulfonylated 1-adamantylamines

HANS-HEINRICH PRÖHL, MARTINA NÄVEKE, PETER G. JONES\* AND ARMAND BLASCHETTE\*

*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

(Received 19 July 1999; accepted 9 September 1999)

### Abstract

*N,N*-Disulfonylated 1-adamantylamines, hitherto elusive, can easily be prepared by reacting 1-bromoadamantane with silver disulfonylamides suspended in anhydrous benzene. Structures have been determined for *N,N*-bis(methanesulfonyl)-1-adamantylamine, C<sub>12</sub>H<sub>21</sub>NO<sub>4</sub>S<sub>2</sub>, *N,N*-bis(*p*-toluenesulfonyl)-1-adamantylamine, C<sub>24</sub>H<sub>29</sub>NO<sub>4</sub>S<sub>2</sub>, and 2-(1-adamantyl)-1,1,3,3-tetraoxo-1,3,2-benzodithiazole [*N*-(1-adamantyl)-*o*-benzenesulfonylimide], C<sub>16</sub>H<sub>19</sub>NO<sub>4</sub>S<sub>2</sub>. Prominent features in the molecular structures are the nearly planar central CNS<sub>2</sub> groupings and the exceptionally long Nsp<sup>2</sup>—Csp<sup>3</sup> bonds (1.53–1.56 Å).

† Part CXX: Friedrichs & Jones (1999).

### Comment

Substitution and elimination reactions of compounds containing the disulfonylamino (disulfonimide) leaving group, –N(SO<sub>2</sub>R)<sub>2</sub>, have aroused considerable attention. Thus, a simple and versatile deamination process for primary aliphatic amines involves electrophilic activation of the C(—N) atom by forming a bis(arenesulfonyl)amine, R'N(SO<sub>2</sub>R)<sub>2</sub>, followed by treatment of this derivative with nucleophiles or by subjecting it to pyrolysis (Baumgarten & Curtis, 1982, and references therein). The disulfonylamines are generally obtained in excellent yields by the reaction of one equivalent of amine with two equivalents of an arenesulfonyl chloride, either in a two-step process requiring isolation of the intermediate sulfonamide, R'NHSO<sub>2</sub>R (DeChristopher *et al.*, 1974), or more economically *via* a one-pot reaction by treating the amine with two equivalents of sulfonyl chloride and two equivalents of NaH in tetrahydrofuran (Bartsch *et al.*, 1977). However, disulfonylamines derived from such sterically hindered molecules as Ph<sub>2</sub>CHNH<sub>2</sub>, *exo*-2-aminonorborene or 1-aminoadamantane could not be prepared, even though the corresponding sulfonamides are readily accessible (Hutchins *et al.*, 1978).

Following an alternative route, we have discovered that *N,N*-disulfonylated 1-adamantylamines, hitherto elusive, can be synthesized in high yields by treating 1-bromoadamantane with silver disulfonylamides, AgN(SO<sub>2</sub>R)<sub>2</sub>, suspended in benzene. It should be noted that this simple procedure is analogous to that used earlier in the synthesis of 1-adamantylsulfonates from 1-haloadamantanes and hexane suspensions of silver sulfonates (Kevill *et al.*, 1970; Takeuchi *et al.*, 1980, 1988). As the silver salts employed in the present work are to some extent soluble in benzene, the aromatic solvent was preferred to hexane [solubilities determined for AgN(SO<sub>2</sub>Me)<sub>2</sub> in benzene: 0.4 g l<sup>-1</sup> at 293 K and 0.9 g l<sup>-1</sup> at 353 K]. Although acetonitrile is known to be an excellent solvent for silver disulfonylamides (Blaschette *et al.*, 1993), it could not be utilized here, as it tends to enter into pseudo-Ritter type reactions with the solutes (Pröhl *et al.*, 1997).

The X-ray crystal structures of three products, *N,N*-bis(methanesulfonyl)-1-adamantylamine, (I), *N,N*-bis(*p*-toluenesulfonyl)-1-adamantylamine, (II), and 2-(1-adamantyl)-1,1,3,3-tetraoxo-1,3,2-benzodithiazole, (III), authenticate them as *N,N*-disulfonylated 1-aminoadamantanes and clearly demonstrate that previous failures to isolate such compounds (Hutchins *et al.*, 1978) cannot be ascribed to an inherent steric incompatibility of a bulky adamantyl cage and two adjacent sulfonyl groups. The molecules are shown in Figs. 1–3, with selected intramolecular geometric data in Tables 1, 3 and 5. Comparable solid-state structures have been reported for seven *N*-alkyl disulfonylamines (Blaschette *et al.*, 1991; Brunzelle *et al.*, 1999; Curtis & Pavkovic, 1983; Henschel *et al.*, 1997; Jones *et al.*, 1995), includ-