du Muséum National d'Histoire Naturelle de lui avoir proposé l'étude de cette molécule et fourni les cristaux.

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des plans moyens, des angles de torsion et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de l'UICr (Référence: PA1183). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Phenyl 2-(Trimethylsilylethynyl)phenyl Ketone and 2-(Trimethylsilylethynyl)benzaldehyde

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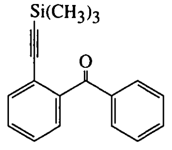
Abstract

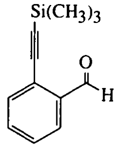
The two aromatic ring planes in phenyl 2-(trimethylsilylethynyl)phenyl ketone, $C_{18}H_{18}OSi$, form a dihedral angle of 67.16 (6)°. The Si atom lies 0.1330 (6) Å out of the plane formed by the disubstituted aromatic ring. The carbonyl unit is not coplanar with either aromatic ring, forming O—C—C—C torsion angles with magnitudes of 41.4 (3) and 33.3 (3)°. The triple bond length is 1.199 (3) Å and the C═O and C—Si bond distances are 1.218 (2) and 1.837 (2) Å, respectively. In 2-(trimethylsilylethynyl)benzaldehyde, $C_{12}H_{14}OSi$, the molecule lies on a crystallographic mirror plane. The triple bond has a length of 1.192 (3) Å and the C═O and C—Si bond distances are 1.196 (3) and 1.839 (3) Å, respectively.

Comment

The title compounds were prepared as part of a structural study involving *o*-carbonyl(ethynyl)benzene derivatives (Garcia & Rodriguez, 1995), which are key intermediates in the synthesis of conjugated ene-yne-[3]-cumulenes, compounds with potential biological activity (Garcia, Ramos, Pratt & Rodriguez, 1995).



(1)



(2)

In phenyl 2-(trimethylsilylethynyl)phenyl ketone, (1), the carbonyl unit is not coplanar with either of the aromatic rings, with torsion angles O—C9—C10—C11 of 33.3 (3)° and O—C9—C8—C7 of 41.4 (3)°. These are somewhat larger than those found in unsubstituted benzophenone, which average 27.8° (Lobanova, 1968; Fleischer, Sung & Hawkinson, 1968). The dihedral angle between the aromatic ring planes is 67.16 (6)°, compared with 56° in benzophenone (Fleischer *et al.*, 1968).

In 2-(trimethylsilylethynyl)benzaldehyde, (2), the molecule lies on a crystallographic mirror plane in the uncommon space group *Ima*2. A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for structures in this space group yielded only 13, of which only two met the strict criteria of Brock & Dunitz (1994) for reliable space group assignment. The mirror is occupied in all 13 structures. The molecules

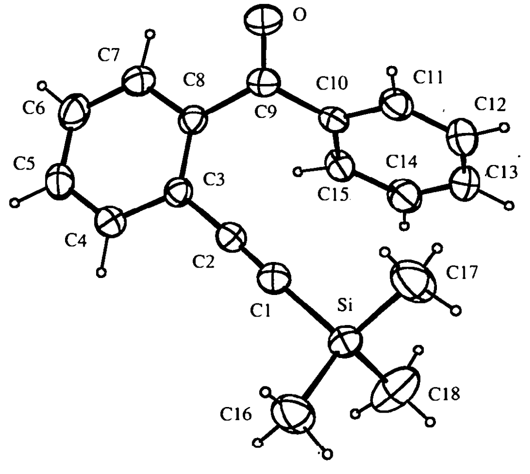


Fig. 1. The molecular structure of (1), with 30% ellipsoids and H atoms of arbitrary radii.

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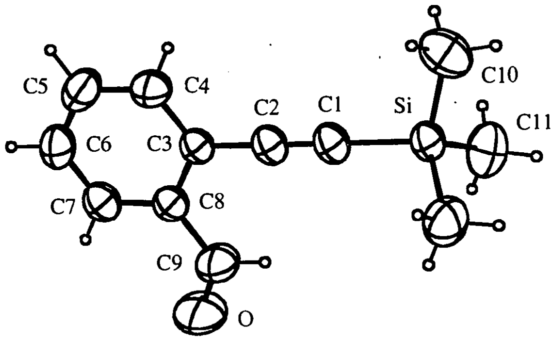
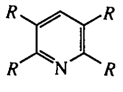
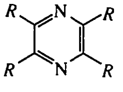


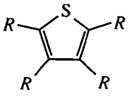
Fig. 2. The molecular structure of (2), with 40% ellipsoids and H atoms of arbitrary radii.

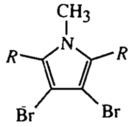
in (2) both stack in the **a** direction, the aromatic rings being required to be parallel by symmetry, but they do not lie directly over one another. The perpendicular distance between them is **a**/2 = 3.550 Å, however, the distance between centroids is 4.077 Å, indicating that the rings are slipped by 2.005 Å from their fully overlapped position.

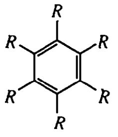
Table 5 shows a comparison of the C1—C2 distances in (1) and (2) with the related compounds shown below.

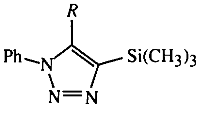

(3)

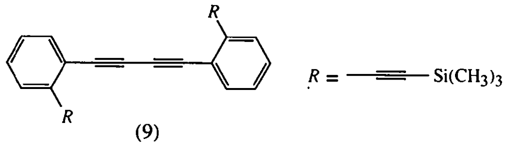

(4)


(5)


(6)


(7)


(8)



(9)

Experimental

The title compounds were prepared by palladium(II)-catalyzed couplings (Austin, Bilow, Kelleghan & Lau, 1981) of trimethylsilylacetylene with 2′-iodoacetophenone (Bacon & Lindsay, 1958) for (1) and with 2-bromobenzaldehyde for (2). The crystal of (2) was mounted in a capillary to prevent sublimation during data collection.

Compound (1)

Crystal data

$C_{18}H_{18}OSi$
$M_r = 278.4$
Monoclinic
$P2_1/c$
$a = 13.801\,(1)$ Å
$b = 10.491\,(1)$ Å
$c = 11.795\,(1)$ Å
$\beta = 105.03\,(1)°$
$V = 1649.4\,(5)$ Å^3
$Z = 4$
$D_x = 1.121$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–11°$
$\mu = 0.131$ mm^{-1}
$T = 296$ K
Fragment
0.45 × 0.38 × 0.30 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4156 measured reflections
3796 independent reflections
2609 observed reflections [$I > 1.0\sigma(I)$]

$R_{\rm int} = 0.023$
$\theta_{\rm max} = 27.47°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: −3.2%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.046$
$S = 1.628$
2609 reflections
254 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\rm max} = 0.03$

$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.08$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.44\,(6) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si	0.56299 (4)	0.17189 (6)	0.22157 (5)	0.0594 (2)
O	0.8687 (1)	0.5240 (2)	0.5500 (1)	0.0885 (6)
C1	0.6375 (1)	0.3185 (2)	0.2321 (2)	0.0571 (6)
C2	0.6890 (1)	0.4119 (2)	0.2411 (2)	0.0487 (5)
C3	0.7482 (1)	0.5255 (2)	0.2467 (1)	0.0444 (5)
C4	0.7256 (1)	0.6092 (2)	0.1516 (2)	0.0556 (6)
C5	0.7780 (2)	0.7205 (2)	0.1534 (2)	0.0644 (7)
C6	0.8523 (2)	0.7525 (2)	0.2509 (2)	0.0690 (7)
C7	0.8746 (1)	0.6734 (2)	0.3467 (2)	0.0615 (6)
C8	0.8251 (1)	0.5578 (2)	0.3459 (2)	0.0458 (5)
C9	0.8533 (1)	0.4759 (2)	0.4530 (2)	0.0531 (6)
C10	0.8666 (1)	0.3367 (2)	0.4411 (1)	0.0448 (5)
C11	0.8449 (1)	0.2552 (2)	0.5236 (2)	0.0586 (6)
C12	0.8580 (2)	0.1266 (2)	0.5153 (2)	0.0747 (8)
C13	0.8931 (2)	0.0779 (2)	0.4265 (2)	0.0775 (8)
C14	0.9170 (2)	0.1568 (2)	0.3457 (2)	0.0726 (7)
C15	0.9030 (1)	0.2862 (2)	0.3524 (2)	0.0556 (6)
C16	0.4348 (2)	0.2065 (3)	0.1328 (2)	0.0873 (9)
C17	0.5614 (2)	0.1229 (3)	0.3719 (2)	0.105 (1)
C18	0.6220 (2)	0.0496 (3)	0.1487 (3)	0.116 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Si—C1	1.837 (2)	C6—C7	1.371 (3)
Si—C16	1.844 (2)	C7—C8	1.390 (3)
Si—C17	1.852 (3)	C8—C9	1.494 (3)
Si—C18	1.847 (3)	C9—C10	1.482 (3)
O—C9	1.218 (2)	C10—C11	1.385 (3)
C1—C2	1.199 (3)	C10—C15	1.379 (3)
C2—C3	1.436 (3)	C11—C12	1.368 (3)
C3—C4	1.394 (3)	C12—C13	1.361 (4)

C3—C8	1.403 (2)	C13—C14	1.365 (3)
C4—C5	1.371 (3)	C14—C15	1.376 (3)
C5—C6	1.369 (3)		
C1—Si—C16	108.2 (1)	C3—C8—C7	118.7 (2)
C1—Si—C17	108.3 (1)	C3—C8—C9	122.8 (2)
C1—Si—C18	107.8 (1)	C7—C8—C9	118.4 (1)
C16—Si—C17	110.5 (1)	O—C9—C8	119.9 (2)
C16—Si—C18	110.3 (1)	O—C9—C10	120.1 (2)
C17—Si—C18	111.7 (1)	C8—C9—C10	119.9 (2)
Si—C1—C2	177.8 (2)	C9—C10—C11	119.2 (2)
C1—C2—C3	177.5 (2)	C9—C10—C15	121.9 (2)
C2—C3—C4	118.7 (1)	C11—C10—C15	118.9 (2)
C2—C3—C8	122.5 (2)	C10—C11—C12	120.2 (2)
C4—C3—C8	118.8 (2)	C11—C12—C13	120.3 (2)
C3—C4—C5	121.2 (2)	C12—C13—C14	120.5 (2)
C4—C5—C6	119.9 (2)	C13—C14—C15	119.7 (2)
C5—C6—C7	120.2 (2)	C10—C15—C14	120.4 (2)
C6—C7—C8	121.1 (2)		

Compound (2)

Crystal data

$C_{12}H_{14}OSi$
$M_r = 202.3$
Orthorhombic
*Ima*2
$a = 7.1006$ (5) Å
$b = 16.880$ (2) Å
$c = 10.1754$ (5) Å
$V = 1219.6$ (3) Å^3
$Z = 4$
$D_x = 1.102$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 25$–41°
$\mu = 1.43$ mm^{-1}
$T = 297$ K
Prism
0.50 × 0.45 × 0.32 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.9235$, $T_{\max} = 0.9955$
2495 measured reflections
1150 independent reflections
1139 observed reflections $[I > 1.0\sigma(I)]$

$R_{\rm int} = 0.023$
$\theta_{\max} = 74.84°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: −2.0%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.043$
$S = 2.289$
1139 reflections
82 parameters
H atoms included but not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o{}^4]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.204(8) \times 10^{-4}$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
Absolute configuration: refinement of the structure with the opposite direction of the polar axis yielded $R = 0.040$, $wR = 0.053$, $S = 2.873$ and uncertainties on refined parameters which were *ca* 25% higher

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si	1/4	0.35315 (3)	0	0.0602 (1)
O	1/4	0.7007 (1)	0.1934 (3)	0.122 (1)
C1	1/4	0.4178 (1)	0.1455 (3)	0.0670 (6)
C2	1/4	0.4604 (1)	0.2389 (2)	0.0599 (6)
C3	1/4	0.5108 (1)	0.3536 (2)	0.0521 (4)
C4	1/4	0.4782 (1)	0.4774 (3)	0.0690 (6)
C5	1/4	0.5260 (2)	0.5887 (3)	0.0797 (8)
C6	1/4	0.6070 (2)	0.5765 (3)	0.0738 (7)
C7	1/4	0.6398 (1)	0.4558 (3)	0.0675 (6)
C8	1/4	0.5935 (1)	0.3423 (2)	0.0566 (5)
C9	1/4	0.6308 (1)	0.2124 (3)	0.087 (1)
C10	1/4	0.2497 (2)	0.0550 (5)	0.115 (1)
C11	0.4617 (4)	0.3744 (1)	−0.0999 (2)	0.0992 (7)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

Si—C1	1.839 (3)	C3—C8	1.402 (3)
Si—C10	1.833 (3)	C4—C5	1.391 (4)
Si—C11	1.850 (3)	C5—C6	1.374 (4)
O—C9	1.196 (3)	C6—C7	1.347 (4)
C1—C2	1.192 (3)	C7—C8	1.394 (3)
C2—C3	1.444 (3)	C8—C9	1.464 (4)
C3—C4	1.375 (3)		
C1—Si—C10	108.6 (2)	C3—C4—C5	120.9 (2)
C1—Si—C11	109.11 (9)	C4—C5—C6	120.3 (3)
C10—Si—C11	110.6 (1)	C5—C6—C7	119.4 (3)
C11—Si—C11′†	108.7 (1)	C6—C7—C8	121.7 (2)
Si—C1—C2	179.2 (2)	C3—C8—C7	119.4 (2)
C1—C2—C3	178.9 (2)	C3—C8—C9	120.2 (2)
C2—C3—C4	120.4 (2)	C7—C8—C9	120.5 (2)
C2—C3—C8	121.3 (2)	O—C9—C8	124.8 (3)
C4—C3—C8	118.3 (2)		

† Atom C11 is related to atom C11′ by the operation ($\frac{1}{2} - x, y, z$).

Table 5. C1—C2 *distances in* (1), (2) *and related compounds*

Compound	C1—C2 (Å)	Reference
(1)	1.199 (3)	This work
(2)	1.192 (3)	This work
(3)	1.190 (4), 1.191 (4)	Garcia, Fronczek & Vollhardt (1995)
(4)	1.198 (5), 1.199 (6)	Garcia, Fronczek & Vollhardt (1995)
(5)	1.190 (4), 1.190 (4)	Garcia, Fronczek & Vollhardt (1995)
(6)	1.189 (5), 1.194 (4)	Garcia, Fronczek & Vollhardt (1995)
(7)	1.195 (3)	Diercks *et al.* (1986)
(8)	1.173 (12), 1.180 (13)	Bettison *et al.* (1988)
(9)	1.194	Guo *et al.* (1994)

C—H distances for (1) range from 0.89 (3) to 1.01 (3) Å. $B_{\rm iso}$ values for these H atoms range from 4.4 (4) to 7.5 (6) Å^2 for the phenyl H atoms and from 10.8 (7) to 18 (1) Å^2 for the methyl H atoms.

For both compounds, data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structures: direct methods (*MULTAN*: Main *et al.*, 1980) for (1); Patterson and Fourier techniques for (2). For both compounds, program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN CIF IN*.

The purchase of the diffractometer was made possible by National Science Foundation chemical instrumentation grants, which we gratefully acknowledge.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Trimer from 5,5-Dimethylcyclohexan-1,3-dione Containing an O-Protonated Furan Ring

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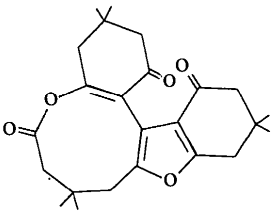
(*Received 23 May 1995; accepted 7 July 1995*)

Abstract

Reaction of 5,5-dimethylcyclohexan-1,3-dione with ammonia in ethanol gave a trimer, 1,2,3,4,6,7,8,9,11,12,13,14-dodecahydro-3,3,8,8,12,12-hexamethyl-1,6,14-trioxobenzo[*b*]benzo[4,5]furo[3,2-*d*]oxoninium hydroxide, $C_{24}H_{31}O_5^+.0.41OH^-$, containing a nine-membered lactone ring and a furan as well as two cyclohexane groups. The furan ring is partially protonated at the O atom with a disordered hydroxide counterion.

Comment

β-Diketones are among the classic ligands of inorganic chemistry but there have been few attempts to prepare complexes of metal ions with cyclic β-diketones such as cyclohexane-1,3-dione (CHD), where the bridgehead methine C2 must present severe steric problems for chelation and bridging between metals is more likely. Colour changes in solution and some early equilibrium studies (Luehrs, Iwamoto & Kleinberg, 1965) indicate that complexes do form but as yet only very poor quality crystals have been obtained in our laboratory. Structures of CHD and of several substituted forms have been reported. These show that the enol form, which predominates in solution, is also found in the solid state (Singh & Calvo, 1975; Etter, Urbanczyk-Lipkowska, Jahn & Frye, 1986; Katrusiak, 1990; Barnes, 1995). The title compound, (I), was the unexpected result of an attempt to crystallize an ammonium salt of dimedone, 5,5-dimethyl-CHD. Ring opening and ring fusion have produced a trimer containing a nine-membered lactone ring and a furan as well as two cyclohexane groups.



(I)

Excluding the peripheral methyl groups, all but three of the non-H atoms can be fitted by only three planes, *A* (O6, C7, C8, O26), *B* (C10, C11, O12, C13, C14, C16, C17, C18, C19, C20, O29) and *C* (C1, C2, C4, C5, O6, C19, C20, O21) with r.m.s. deviations 0.035, 0.054 and 0.060 Å, respectively. The maximum deviation is 0.108 Å for C20. The angle between *A* and *B* is 19.29 (8)°, and between *B* and *C* is 86.35 (4)°. The nine-membered lactone can be described as an eight-membered tub plus C9 forming a prow to place the methyl groups C24 and C25 *exo* to the ring. The angle between the base of the tub (O6, C7, C11, C19) and the prow (C8, C9, C10) is 5.5 (1)°.

No pK_a value is available for the very weakly basic O atom in the furan. Protonation usually occurs not at an O atom but at an α-C atom (Joule, Mills & Smith, 1995). NMR data show protonation at carbon to give a stable cation from 2,5-di-*tert*-butylfuran in solution (Carmody *et al.*, 1976). In (I), there is clear evidence for