Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cyclohepta-3,5-dien-1-yl 3,5-Dinitrobenzoate

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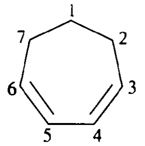
Abstract

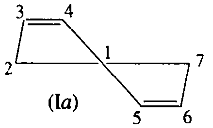
The cyclohepta-3,5-diene ring in the title compound, $C_{14}H_{12}N_2O_6$, is the first example of a 'free' ring to be characterized by crystal structure analysis. All previous examples are either bridged, fused to other rings or have exocyclic conjugative substituents attached to the ring sp^2-C atoms. All but one of these examples adopts the C_2-symmetric (twist) conformation, despite the fact that experimental gas-phase and computational results show a C_s-symmetric (envelope) conformation for the free ring. The 'free' cyclohepta-3,5-diene in the title compound clearly adopts a C_s-symmetric conformation with C1 displaced from the plane of the other six ring atoms. The ring is forced to adopt the C_2-symmetric conformation in more complex systems so as to minimize unfavourable intramolecular non-bonded repulsions.

Comment

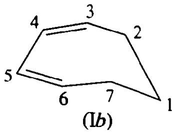
Cyclohepta-3,5-diene, (I), has been studied by a variety of experimental and computational techniques. Crews (1971) interpreted NMR data in terms of a distorted twist conformation (I*a*) of C_2 symmetry. However, electron diffraction (Chiang & Bauer, 1966; Hagen & Traetteberg, 1972) and microwave data (Avirah, Molloy & Cook, 1979) were interpreted unequivocally in terms of a C_s-symmetric conformation (I*b*), having all atoms except C1 coplanar. Molecular-mechanics calculations by Burkert & Allinger (1982) and by Favini, Maggi & Todeschini (1983) indicated that the experimentally observed C_s form (I*b*) was energetically preferred by 7–8 kJ mol^{-1} over the C_2 form (I*a*). This result was almost exactly reproduced by Saebo & Boggs (1982) using *ab initio* methods.



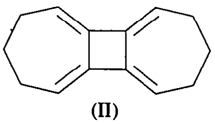
(I)



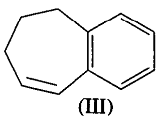
(I*a*)



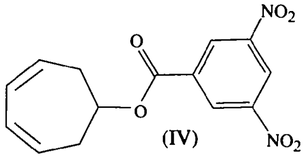
(I*b*)



(II)



(III)



(IV)

Recently (Allen, Garner, Howard & Pitchford, 1994), we performed a conformational analysis of non-bridged examples of (I) using available crystallographic results from the Cambridge Structural Database (Allen *et al.*, 1991, hereinafter CSD). To our initial surprise we found that 13 of the 20 crystallographic observations of (I) adopted the C_2-symmetric conformation (I*a*). A further six examples were distorted by small-ring fusion at the 1–2 bond and exhibited a conformation that is typical of cyclohepta-1,3,5-trienes. Only one example, the symmetrically related ring in (II), adopted the energetically preferred C_s conformation (I*b*). Closer examination of the 13 C_2 conformers showed that in ten cases either one (seven examples) or both (three examples) of the 'double' bonds in (I) arose from benzo-fusion

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(*i.e.* we had equated double and aromatic links between sp^2-C atoms in our CSD searches). Further, in the seven mono-fused systems, the second double bond was part of a conjugated system involving —C═O, —C═C or phenyl substituents. In the three remaining non-fused examples of the C_2 conformer, either one or both of the double bonds was similarly conjugated to exocyclic substituents. Our own molecular-mechanics calculations [fully described by Allen *et al.* (1994)] reconfirmed the energetic preference for the C_s form over the C_2 form for parent (I), but showed that this preference was clearly reversed for the mono-benzo model compound (III). It would appear that the *ca* 45° torsion angle about the C═C—C═C (4–5) single bond in the C_2 form minimizes unfavourable H···H non-bonded interactions, as in benzocycloheptene (Allinger & Sprague, 1972). Since the CSD contains no unbridged examples of (I) where the double bonds are neither benzo-fused nor connected to conjugative substituents, then parent (I) remains uncharacterized by crystal structure analysis. Thus, we have sought to synthesize and crystallize suitable model compounds to fill a gap in the crystallographic literature that has been revealed by our CSD-based conformational analysis.

The 1-substituent in the title compound, (IV), is placed as far as possible from the 3,5-diene system and the molecular structure of (IV) (Fig. 1) shows quite clearly that the cyclohepta-3,5-diene ring now adopts the C_s conformation (I*b*). Atoms C2—C3—C4—C5—C6—C7 form an approximate plane with an r.m.s. deviation of only 0.06 Å from the mean plane. C1 is significantly displaced from this mean plane by 0.730 (4) Å. This result is in complete accord with both the gas-phase experimental data and with the molecular-mechanics and *ab initio* calculations for the free ring (I).

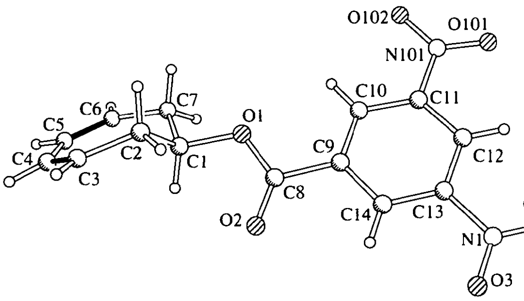

Fig. 1. A perspective view of the title compound showing the C_s-symmetric (envelope) conformation of the cyclohepta-3,5-diene ring (C1–C7).

In Table 3 we compare the intra-annular torsion angles in (IV) with the *ab initio* results. The C_s-symmetric conformer in (IV) has the C═C—C═C (4–5) torsion angle close to zero: the normal arrangement that permits conjugation between the double bonds. As a result, the C4—C5 bond at 1.450 (5) Å is typical of conjugated C_{sp^2}—C_{sp^2} single bonds, which have a standard mean value of 1.455 (2) Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). This contrasts with a mean C4—C5 bond length of 1.484 (4) Å between ethylenic sp^2-C atoms in three C_2 conformers from the CSD that exhibit a mean C═C—C═C torsion angle of 43.7 (9)°.

A more general result of this work is that surveys of the current contents of the crystallographic databases can indicate areas of chemistry that are not well covered in the existing crystallographic literature. Such an approach to the selection of structures for crystal structure analysis, and for collaborative ventures between synthetic chemists and crystallographers, may prove to be extremely fruitful in the future.

Experimental

The compound cyclohepta-3,5-dien-1-yl 3,5-dinitrobenzoate, (IV), was prepared by the reaction of 3,5-cycloheptadienol (Johnson, Golebiowski & Steensma, 1992) with 2,4-dinitrobenzoylchloride (1.2 equivalents) and triethylamine (2.5 equivalents) in anhydrous dichloromethane, from 273 K to room temperature. On completion of the reaction, ether and water were added and the organic layer was separated, washed with water and brine, dried over magnesium sulfate and concentrated. The title ester was obtained in 85% yield by flash column chromatography (eluant light petroleum ether:ethyl acetate 9:1). Crystals of (IV), m.p. 350.5–351.0 K, were grown by slow diffusion of hexane into a concentrated solution of the ester in ethyl acetate. Elemental analysis: found C 54.6, H 4.32, N 9.09%; calculated for $C_{14}H_{12}N_2O_6$ C 55.3, H 3.98, N 9.21%. EI mass spectrum (*m*/*z*, relative intensity): 305 (MH^+, 0.9), 304 (M^+, 3.1), 183 (11), 92 (100), 75 (11), 51 (16) a.m.u. (%). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 9.22 [1H, *m*, Ar—H(C4)], 9.13 [2H, *m*, Ar—H(C2,6)], 5.95 (2H, *m*, C═C—H), 5.78 (2H, *m*, H—C═C), 5.48 (1H, quintet J = 6.5 Hz, CHOCOAr), 2.75 (4H, *dd*, J = 6.5, 8 Hz, —CH_2) p.p.m. ^{13}C NMR (50 MHz, $CDCl_3$, 298 K): δ 161.6, 148.6, 134.3, 129.4, 127.1, 126.6, 122.3, 75.5, 35.9 p.p.m. IR (CsI disk): ν_{max} 1729, 1629, 1549, 1346, 1279, 1171, 1076, 922 cm^{-1}.

Crystal data

$C_{14}H_{12}N_2O_6$
M_r = 304.26
Monoclinic
$P2_1/n$
a = 6.7210 (10) Å
b = 9.002 (2) Å
c = 22.914 (5) Å
β = 91.46 (3)°
V = 1385.9 (5) Å^3
Z = 4
D_x = 1.458 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.5–15°
μ = 0.116 mm^{-1}
T = 150.0 (2) K
Hexagonal column
0.50 × 0.30 × 0.30 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer with Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)

2438 independent reflections
1618 observed reflections
[$I > 2\sigma(I)$]
R_{int} = 0.041
θ_{max} = 25.05°

ω–2θ scans
Absorption correction:
ψ scans (*TEXSAN*; Molecular Structure Corporation, 1993)
$T_{\min} = 0.83$, $T_{\max} = 1.00$
2661 measured reflections

$h = 0 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = -27 \rightarrow 27$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0518$
$wR(F^2) = 0.1431$
$S = 1.168$
2320 reflections
199 parameters
H atoms placed in idealized positions and thereafter allowed to ride on their parent C atoms

$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2 + 0.4618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.064$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
C1	0.1692 (4)	0.1921 (3)	0.96437 (11)	0.0304 (7)
C2	0.2704 (5)	0.3371 (3)	0.98135 (12)	0.0366 (7)
C3	0.2744 (5)	0.3640 (3)	1.04592 (13)	0.0420 (8)
C4	0.1322 (5)	0.3296 (3)	1.08373 (13)	0.0414 (8)
C5	−0.0635 (5)	0.2667 (3)	1.07217 (14)	0.0422 (8)
C6	−0.1470 (5)	0.2138 (3)	1.02295 (13)	0.0382 (7)
C7	−0.0553 (4)	0.1941 (3)	0.96451 (13)	0.0375 (7)
C8	0.3833 (4)	0.0812 (3)	0.89432 (12)	0.0298 (7)
C9	0.3983 (4)	0.0323 (3)	0.83188 (12)	0.0279 (6)
C10	0.2440 (4)	0.0564 (3)	0.79128 (11)	0.0273 (6)
C11	0.2663 (4)	0.0069 (3)	0.73452 (11)	0.0272 (6)
C12	0.4354 (4)	−0.0660 (3)	0.71640 (12)	0.0316 (7)
C13	0.5837 (4)	−0.0897 (3)	0.75830 (13)	0.0320 (7)
C14	0.5700 (4)	−0.0418 (3)	0.81552 (12)	0.0320 (7)
O1	0.2146 (3)	0.1551 (2)	0.90315 (8)	0.0310 (5)
O2	0.5107 (3)	0.0543 (2)	0.93087 (9)	0.0410 (5)
O3	0.8987 (3)	−0.1872 (2)	0.77612 (10)	0.0457 (6)
O4	0.7605 (3)	−0.2233 (3)	0.69053 (10)	0.0526 (6)
N1	0.7607 (4)	−0.1728 (3)	0.74026 (12)	0.0392 (6)
N101	0.1036 (4)	0.0294 (3)	0.69128 (10)	0.0343 (6)
O101	0.1220 (4)	−0.0247 (3)	0.64272 (9)	0.0570 (7)
O102	−0.0433 (3)	0.0991 (2)	0.70643 (9)	0.0372 (5)

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

C1—O1	1.482 (3)	C9—C10	1.393 (4)
C1—C7	1.509 (4)	C10—C11	1.386 (4)
C1—C2	1.518 (4)	C11—C12	1.385 (4)
C2—C3	1.499 (4)	C11—N101	1.471 (4)
C3—C4	1.342 (5)	C12—C13	1.383 (4)
C4—C5	1.450 (5)	C13—C14	1.386 (4)
C5—C6	1.335 (4)	C13—N1	1.473 (4)
C6—C7	1.499 (4)	O3—N1	1.230 (3)
C8—O2	1.207 (3)	O4—N1	1.227 (3)
C8—O1	1.334 (3)	N101—O101	1.224 (3)
C8—C9	1.503 (4)	N101—O102	1.228 (3)
C9—C14	1.393 (4)		
O1—C1—C7	103.6 (2)	C12—C11—C10	122.9 (3)
O1—C1—C2	109.5 (2)	C12—C11—N101	117.7 (2)
C7—C1—C2	115.5 (3)	C10—C11—N101	119.4 (2)
C3—C2—C1	112.9 (2)	C13—C12—C11	116.6 (3)
C4—C3—C2	127.2 (3)	C12—C13—C14	123.0 (3)
C3—C4—C5	129.0 (3)	C12—C13—N1	117.1 (3)
C6—C5—C4	130.8 (3)	C14—C13—N1	119.8 (3)
C5—C6—C7	128.6 (3)	C13—C14—C9	118.6 (3)
C6—C7—C1	115.9 (2)	C8—O1—C1	116.9 (2)
O2—C8—O1	125.8 (3)	O4—N1—O3	124.4 (3)
O2—C8—C9	122.6 (3)	O4—N1—C13	117.8 (3)
O1—C8—C9	111.6 (2)	O3—N1—C13	117.8 (3)
C14—C9—C10	120.2 (3)	O101—N101—O102	124.1 (2)
C14—C9—C8	118.2 (2)	O101—N101—C11	117.9 (2)
C10—C9—C8	121.6 (2)	O102—N101—C11	118.0 (2)
C11—C10—C9	118.7 (3)		

Table 3. *Intra-annular torsion angles* (°) *for the cyclohepta-3,5-diene ring in* (IV) *determined by X-ray diffraction compared with results from ab initio methods* (*Saebo & Boggs*, 1982)

	X-ray	*ab initio*
C7—C1—C2—C3	77.6 (3)	70.5
C1—C2—C3—C4	−36.6 (5)	−30.4
C2—C3—C4—C5	−3.9 (5)	1.4
C3—C4—C5—C6	7.2 (6)	0.0
C4—C5—C6—C7	4.6 (6)	−1.4
C5—C6—C7—C1	18.9 (5)	30.4
C6—C7—C1—C2	−66.2 (3)	−70.5

The structure was solved using *SHELXTL-Plus* (Sheldrick, 1991) and refined using *SHELXL93* (Sheldrick, 1993) with anisotropic displacement parameters allowed for all non-H atoms. Refinement was on F^2 for all reflections except 118 with very negative F^2 or flagged by the user for potential systematic errors. No disorder or unusual features were noted.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1949–1950

(*Z*)-*N*-[(2*R*,3*R*)-2-(*tert*-Butoxycarbonylamino)-3-(*tert*-butyldiphenylsiloxy)butylidene]benzylamine *N*-Oxide

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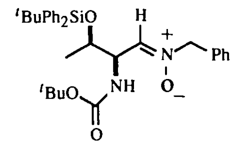
Abstract

The title compound, $C_{32}H_{42}N_2O_4Si$, is a key intermediate in the stereoselective synthesis of α,β-diaminoaldehydes, α,β-diaminoacids and chiral 1,2-diamines. The X-ray structure determination shows that the nitrone [C—CH=N$^+$(O$^-$)—C] system is planar with torsion angles of 175 (H1—C1—N1—O1) and 175.0° (C2—C1—N1—C5).

Comment

As part of a project directed toward the synthesis of chiral α,β-diaminoaldehydes, α,β-diaminoacids and 1,2-diamines, we described a stereodivergent procedure in which chiral nitrones derived from natural α-amino acids were used as suitable starting materials. The arrangement of the protecting groups in the nitrone is crucial for the selectivity of the process (Dondoni, Merchan, Merino, Tejero & Bertolasi, 1994).

Study the interaction of the nitrone functionality with its vicinal groups should aid the elucidation of the reactivity of the title nitrone, (I), derived from L-threonine. The present structure analysis shows that a plausible hydrogen bond O1···H(N2) is, in fact, impossible as a result of the bulkiness of the *tert*-butyldiphenylsilyl group. The molecular geometry and numbering scheme are shown in Fig. 1. The *Z* configuration of the nitrone is confirmed, as well as the planarity of the important nitrone atoms C1, H1, N1 and O1. Atoms C2 and C5 are also coplanar with the nitrone moiety.



(I)

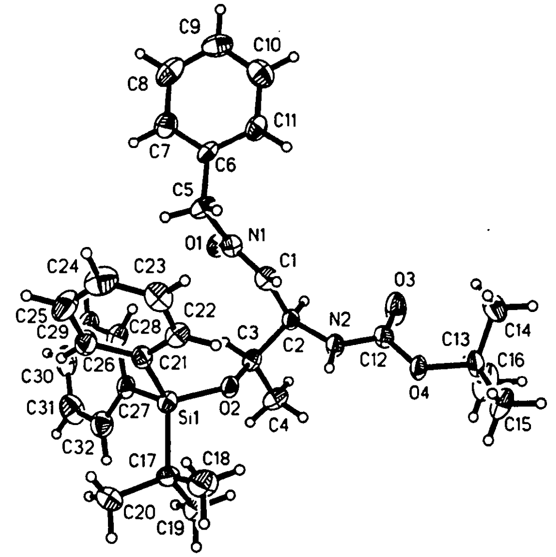


Fig. 1. Molecular configuration and atom-numbering scheme of the title compound. Displacement ellipsoids are plotted at the 30% probability level.

Experimental

The synthesis was carried out by reaction of the corresponding aldehyde with *N*-benzylhydroxylamine by the method described previously (Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994). The compound was purified by column chromatography and crystals suitable for X-ray experiments were obtained by slow evaporation of the solvents [m.p. = 400 K; $[\alpha]_D = -24.3°$ (c 1.2 g 100 ml^{-1}, chloroform)].

Crystal data

$C_{32}H_{42}N_2O_4Si$
$M_r = 546.77$
Orthorhombic
$P2_12_12_1$
$a = 10.002\,(2)$ Å
$b = 14.274\,(3)$ Å
$c = 21.976\,(4)$ Å
$V = 3137.5\,(11)$ Å^3
$Z = 4$
$D_x = 1.158$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 9.45$–$21.85°$
$\mu = 0.111$ mm^{-1}
$T = 293\,(2)$ K
Transparent block
0.5 × 0.3 × 0.2 mm
Colourless

Data collection

Siemens *P*4 diffractometer
Profile data from $2\theta/\omega$ scans
Absorption correction: semi-empirical (ellipsoidal) refined from ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.652$, $T_{\max} = 0.841$
3015 measured reflections
2827 independent reflections

1648 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0633$
$\theta_{\max} = 22.50°$
$h = -1 \rightarrow 10$
$k = -1 \rightarrow 15$
$l = -1 \rightarrow 23$
3 standard reflections monitored every 97 reflections
intensity decay: 7.26%