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## Half-Chair Conformation of *trans*-1,4-Dimethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione

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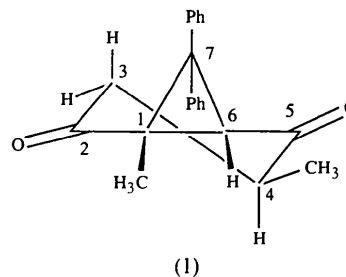
### Abstract

The structure of the title compound, C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>, was determined by X-ray analysis. The results revealed that the 2,5-dioxocyclohexane skeleton is in a half-chair conformation, with torsion angles C(2)—C(3)—C(4)—C(5) −1.5 (3) and C(2)—C(3)—C(4)—C(5) −36.5 (3)° on account of the fused cyclopropane ring which locates the 4-methyl group in an equatorial position. The plane of the *endo*-phenyl group was also found to be essentially parallel to the fused C(1)—C(6) bond.

### Comment

The title compound, (1), was synthesized by the photo-induced hydrogenation of 2,5-dimethyl-1,1-diphenylhomobenzoquinone (Oshima, Tamada & Nagai, 1994). It underwent a fast H/D exchange at both the 3- and 4-positions when treated with methanol-*[d]*<sub>4</sub>. This means that the more stable configuration and conformation. An NMR study showed that the vicinal coupling constants of the 4-methine proton are *J* = 13.86 and 6.60 Hz with the adjacent methylene H atoms, suggesting a

possible staggered conformation around the C(3)—C(4) bond (Hoch, Dobson & Karplus, 1985). However, the conjunction with the rigid cyclopropane ring seems to exert some steric effects on the conformation of the parent six-membered ring. Such effects would result in the deformation of the relevant ring system from the familiar chair form. Therefore, some ambiguity remains in the structure deduced from the NMR spectrum. In addition, compound (1) consists of a 2,5-dioxonorcarane framework with two trigonal carbonyl Csp<sup>2</sup> atoms for which the structural features are not well known. The X-ray structure analysis of (1) was thus carried out.



The X-ray crystal structure of (1) showed that the six-membered 2,5-dioxocyclohexane framework adopts a half-chair conformation, with torsion angles C(1)—C(2)—C(3)—C(4) 34.7 (3), C(2)—C(3)—C(4)—C(5) −36.5 (3), C(3)—C(4)—C(5)—C(6) 20.4 (3), C(4)—C(5)—C(6)—C(1) −1.7 (3), C(2)—C(1)—C(6)—C(5) −1.5 (3) and C(6)—C(1)—C(2)—C(3) −15.1 (3)°, owing to the fused cyclopropane ring. Therefore, the larger coupling constant (13.86 Hz) can be ascribed to the axial-H(3A)—axial-H(4) coupling and the smaller (6.60 Hz) to the equatorial-H(3B)—axial-H(4) coupling, as indicated by the torsion angles H(3A)—C(3)—C(4)—H(4) −154.4 (4) and H(3B)—C(3)—C(4)—H(4) −37.0 (3)°.

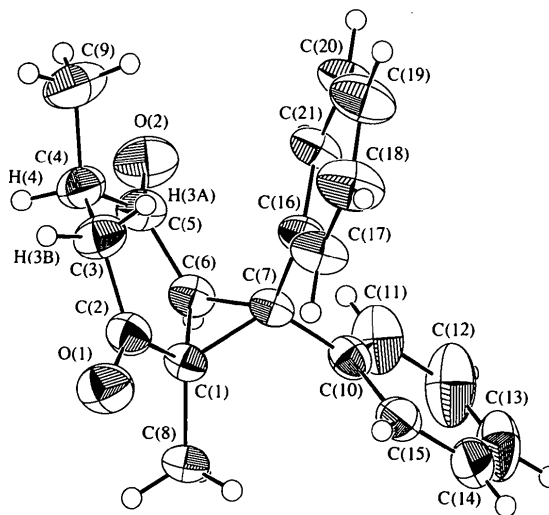


Fig. 1. A view of the title molecule with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The unexpected high field shift of the axial H(3A) proton ( $\delta$  1.12 p.p.m.) relative to the equatorial H(3B) proton ( $\delta$  2.34 p.p.m.) in CDCl<sub>3</sub> is of interest. Taking into account that the cyclohexanone  $\alpha$ -axial and  $\alpha$ -equatorial protons of 5 $\beta$ -androsterane-3,17-dione resonate at 1.39 and 2.05, and 2.02 and 2.69 p.p.m., respectively (Breitmaier & Voelter, 1987), the high field absorption of the axial H(3A) proton may be rationalized by the conformational locking of the *endo*-phenyl group so as to shield the facing axial position magnetically. In fact, the *endo*-phenyl ring is located in such a way that the aromatic plane is almost parallel to the opposite cyclopropane C(1)—C(6) bond [the angle between the C(16)—C(21) plane and the C(1)—C(6) bond is 4.8°] and hence is very close to the axial H(3A) atom as is evident from the short interatomic distances (2.61–3.69 Å) between the H(3A) atom and each of the six aromatic C atoms

## Experimental

The title compound, (1), was synthesized by the photoinduced hydrogenation of 2,5-dimethyl-1,1-diphenylhomobenzoquinone (Oshima, Tamada & Nagai, 1994) in the presence of triethylamine (Moriwaki, Matsumoto, Nagai & Oshima, 1996).

### Crystal data

C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 304.37  
 Monoclinic  
*P*2<sub>1</sub>/*a*  
*a* = 8.925 (4) Å  
*b* = 23.480 (12) Å  
*c* = 8.049 (3) Å  
 $\beta$  = 96.36 (3)°  
*V* = 1676 (1) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.21 Mg m<sup>-3</sup>  
*D<sub>m</sub>* = 1.21 Mg m<sup>-3</sup>  
*D<sub>m</sub>* measured by flotation in  
*n*-hexane/CCl<sub>4</sub>

### Data collection

Mac Science MXC3 diffractometer  
 $\theta/\omega$  scans  
 Absorption correction: empirical,  $\psi$  scans (CRYSTAN; Stewart *et al.*, 1994)  
*T<sub>min</sub>* = 0.817, *T<sub>max</sub>* = 0.998  
 4531 measured reflections  
 3840 independent reflections

### Refinement

Refinement on *F*  
*R* = 0.0699  
*wR* = 0.0709  
*S* = 0.81

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 22 reflections  
 $\theta$  = 15.9–17.5°  
 $\mu$  = 0.071 mm<sup>-1</sup>  
*T* = 296 K  
 Prism  
 0.50 × 0.35 × 0.30 mm  
 Colourless

3340 observed reflections  
 $[F > 3\sigma(F)]$   
*R<sub>int</sub>* = 0.045  
 $\theta_{max}$  = 27.5°  
*h* = 0 → 11  
*k* = -30 → 0  
*l* = -10 → 10  
 3 standard reflections monitored every 100 reflections  
 intensity decay: not significant

( $\Delta/\sigma$ )<sub>max</sub> = 0.0180  
 $\Delta\rho_{max}$  = 0.68 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.42 e Å<sup>-3</sup>  
 Extinction correction: none

2597 reflections  
 228 parameters  
 Only H-atom *U*'s refined  
 $w = \exp(10.0\sin^2\theta/\lambda^2)/a^2(F_o)$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	<i>U<sub>eq</sub></i>
O(1)	0.9667 (3)	0.4727 (1)	0.6955 (4)	0.067
O(2)	0.7183 (4)	0.2646 (1)	0.6329 (5)	0.076
C(1)	0.9684 (2)	0.3864 (1)	0.5495 (3)	0.039
C(2)	0.9002 (3)	0.4295 (1)	0.6541 (3)	0.046
C(3)	0.7465 (3)	0.4188 (1)	0.7101 (4)	0.056
C(4)	0.7078 (3)	0.3573 (1)	0.7492 (4)	0.054
C(5)	0.7672 (3)	0.3130 (1)	0.6383 (4)	0.049
C(6)	0.8969 (2)	0.3272 (1)	0.5419 (3)	0.042
C(7)	0.8736 (2)	0.3656 (1)	0.3894 (3)	0.038
C(8)	1.1372 (2)	0.3913 (1)	0.5487 (3)	0.052
C(9)	0.5384 (4)	0.3501 (2)	0.7624 (7)	0.078
C(10)	0.9555 (2)	0.3486 (1)	0.2430 (3)	0.042
C(11)	0.9602 (6)	0.2917 (2)	0.1942 (5)	0.071
C(12)	1.0342 (8)	0.2767 (2)	0.0574 (5)	0.091
C(13)	1.0993 (5)	0.3170 (2)	-0.0342 (4)	0.080
C(14)	1.0925 (3)	0.3736 (2)	0.0113 (4)	0.062
C(15)	1.0206 (3)	0.3896 (1)	0.1483 (3)	0.050
C(16)	0.7222 (2)	0.3914 (1)	0.3317 (3)	0.040
C(17)	0.7089 (3)	0.4491 (1)	0.2948 (4)	0.053
C(18)	0.5689 (4)	0.4719 (2)	0.2354 (6)	0.071
C(19)	0.4422 (3)	0.4374 (2)	0.2145 (6)	0.072
C(20)	0.4548 (3)	0.3798 (2)	0.2488 (5)	0.061
C(21)	0.5945 (3)	0.3567 (1)	0.3069 (4)	0.049

Table 2. Selected geometric parameters (Å, °)

O(1)—C(2)	1.202 (4)	C(3)—C(4)	1.525 (5)
O(2)—C(5)	1.217 (4)	C(4)—C(5)	1.505 (5)
C(1)—C(2)	1.490 (4)	C(4)—C(9)	1.537 (5)
C(1)—C(6)	1.527 (4)	C(5)—C(6)	1.501 (4)
C(1)—C(7)	1.540 (4)	C(6)—C(7)	1.519 (4)
C(1)—C(8)	1.512 (3)	C(7)—C(10)	1.508 (4)
C(2)—C(3)	1.512 (4)	C(7)—C(16)	1.506 (3)
C(2)—C(1)—C(6)	116.5 (2)	C(4)—C(5)—C(6)	119.7 (3)
C(2)—C(1)—C(7)	117.9 (2)	C(1)—C(6)—C(5)	121.6 (3)
C(2)—C(1)—C(8)	114.8 (3)	C(1)—C(6)—C(7)	60.7 (2)
C(6)—C(1)—C(7)	59.4 (2)	C(5)—C(6)—C(7)	120.4 (2)
C(6)—C(1)—C(8)	118.8 (2)	C(1)—C(7)—C(6)	59.9 (2)
C(7)—C(1)—C(8)	118.4 (2)	C(1)—C(7)—C(10)	118.0 (2)
O(1)—C(2)—C(1)	120.6 (3)	C(1)—C(7)—C(16)	121.4 (2)
O(1)—C(2)—C(3)	119.6 (3)	C(6)—C(7)—C(10)	116.1 (2)
C(1)—C(2)—C(3)	119.7 (3)	C(6)—C(7)—C(16)	121.7 (2)
C(2)—C(3)—C(4)	116.9 (3)	C(10)—C(7)—C(16)	111.2 (2)
C(3)—C(4)—C(5)	115.5 (3)	C(7)—C(10)—C(11)	120.4 (3)
C(3)—C(4)—C(9)	111.4 (3)	C(7)—C(10)—C(15)	120.8 (3)
C(5)—C(4)—C(9)	112.3 (3)	C(7)—C(16)—C(17)	120.7 (2)
O(2)—C(5)—C(4)	121.3 (3)	C(7)—C(16)—C(21)	120.0 (2)
O(2)—C(5)—C(6)	118.9 (3)		

All calculations were performed using *CRYSTAN-GM* software (Gilmore & Brown, 1988).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: OA1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**(1E,3Z,5E)-2,5-Diaza-1,6-bis(dimethyl-amino)-1,3,5-hexatriene-3,4-dicarbonitrile**

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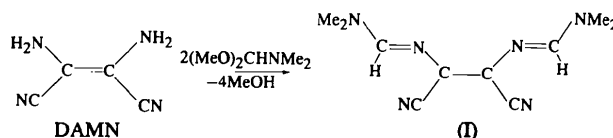
(Received 5 December 1995; accepted 1 April 1996)

**Abstract**

The title structure consists of discrete C<sub>10</sub>H<sub>14</sub>N<sub>6</sub> molecules which have a *cis* configuration and an extended conjugation. The molecules are slightly distorted from planarity.

**Comment**

*N,N*-Dimethylformamide dimethyl acetal reacts as a formylating agent with primary amines providing amidines which may be used in the synthesis of more complex molecules (Abdullah & Brinkmeyer, 1979; Williams & Brown, 1995), for example, *N,N*-dimethylformamide dimethyl acetal is known to react with *o*-phenylenediamine to give benzimidazole (Stanovnik & Tisler, 1974). In contrast, the analogous reaction with diaminomaleonitrile (DAMN) under mild conditions affords bis(amidine) (I), instead of the expected 4,5-dicyanoimidazole heterocycle, in almost quantitative yield. Since the stereochemistry of (I) could not be established definitely on the basis of spectroscopic data, an X-ray analysis was conducted.



The title molecule has a *cis* configuration and an extended conjugation (Fig. 1). Intramolecular bond lengths and angles have usual values. There are no

unusual close intermolecular contacts and the asymmetric unit is not quite planar. The dihedral angles between the planes defined by *A* (C5, N3, C3, N2), *B* (C10, N6, C8, N5) and *C* (N1, C1, C2, C7, C6, N4) are *A/B* 6 (1), *B/C* 8 (1) and *A/C* 3 (2)°.

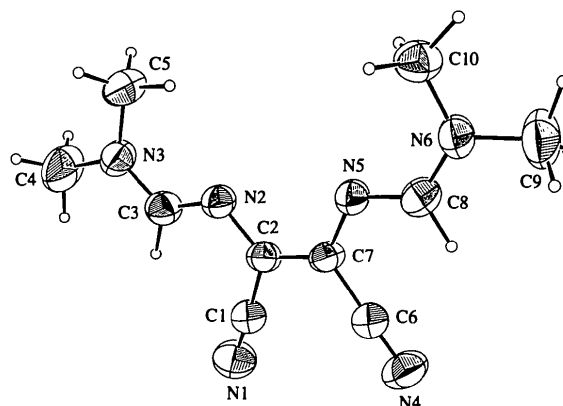


Fig. 1. An ORTEP (Johnson, 1965) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

**Experimental**

A mixture of diaminomaleonitrile (10 g, 92.59 mmol) and *N,N*-dimethylformamide dimethyl acetal (28 ml, 210.08 mmol) in toluene (20 ml) was heated for 1 h in a water bath and for an additional 30 min at 403 K in order to remove the methanol formed. All volatiles were then driven off *in vacuo*. The residual crude brown product was crystallized from dimethyl sulfoxide (35 ml) to afford crystals of the title compound.

*Crystal data*

C<sub>10</sub>H<sub>14</sub>N<sub>6</sub>  
*M<sub>r</sub>* = 218.263  
 Monoclinic  
*P*2<sub>1</sub>/*a*  
*a* = 7.671 (1) Å  
*b* = 20.414 (2) Å  
*c* = 8.326 (2) Å  
 $\beta$  = 112.39 (2)°  
*V* = 1205.6 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.203 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical *via*  $\psi$  scans (*MolEN*; Fair, 1990)  
*T<sub>min</sub>* = 0.967, *T<sub>max</sub>* = 0.998  
 2711 measured reflections  
 2343 independent reflections

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 10.68–18.18°  
 $\mu$  = 0.075 mm<sup>-1</sup>  
*T* = 295 K  
 Prism  
 0.35 × 0.25 × 0.15 mm  
 Brown

1098 observed reflections  
 [*I* > 3 $\sigma$ (*I*)]  
*R<sub>int</sub>* = 0.015  
 $\theta_{\max}$  = 26.32°  
*h* = 0 → 9  
*k* = 0 → 25  
*l* = -10 → 9  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 4.76%