

C7—O1—C1	106.0 (2)	C4—C3—C2	121.0 (3)
C7—O2—C2	108.3 (3)	C3—C4—C5	122.5 (3)
C4—O3—C3	60.7 (2)	O6—C6—C5	101.8 (3)
O1—C1—C2	102.7 (3)	C1—C6—C5	116.9 (3)
C2—C1—C6	116.5 (3)	O1—C7—O2	106.2 (2)
O2—C2—C1	102.4 (3)	C8—C7—C9	112.5 (3)
C1—C2—C3	115.1 (3)	C12—C10—C11	113.8 (4)

C7—O1—C1—C2	-37.6 (3)	O3—C4—C5—O5	166.3 (3)
C7—O1—C1—C6	-162.6 (3)	C3—C4—C5—O5	-125.4 (4)
C7—O2—C2—C1	-19.9 (3)	O3—C4—C5—C6	-78.3 (4)
C7—O2—C2—C3	103.4 (3)	C3—C4—C5—C6	-10.1 (5)
O1—C1—C2—O2	34.9 (3)	C10—O6—C6—C1	-157.9 (3)
C6—C1—C2—O2	155.7 (3)	C10—O6—C6—C5	-35.3 (3)
O1—C1—C2—C3	-85.7 (3)	O1—C1—C6—O6	-174.8 (3)
C6—C1—C2—C3	35.1 (4)	C2—C1—C6—O6	68.6 (4)
C4—O3—C3—C2	-112.4 (3)	O1—C1—C6—C5	72.7 (4)
O2—C2—C3—O3	-62.4 (4)	C2—C1—C6—C5	-43.9 (4)
C1—C2—C3—O3	53.4 (4)	O5—C5—C6—O6	35.4 (3)
O2—C2—C3—C4	-130.8 (3)	C4—C5—C6—O6	-84.7 (3)
C1—C2—C3—C4	-15.0 (4)	O5—C5—C6—C1	150.2 (3)
C3—O3—C4—C5	115.0 (4)	C4—C5—C6—C1	30.1 (5)
C2—C3—C4—O3	103.3 (3)	C1—O1—C7—O2	25.6 (3)
O3—C3—C4—C5	-100.5 (4)	C2—O2—C7—O1	-2.5 (4)
C2—C3—C4—C5	2.8 (5)	C5—O5—C10—O6	2.1 (4)
C10—O5—C5—C4	99.4 (4)	C6—O6—C10—O5	21.7 (4)
C10—O5—C5—C6	-23.4 (4)		

Data collection: XSCANS (Siemens, 1993). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976) in PLATON98 (Spek, 1990, 1998). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1231). Services for accessing these data are described at the back of the journal.

## References

- Angyal, S. J. & Matheson, N. K. (1955). *J. Am. Chem. Soc.* **77**, 4343–4346.
- Chung, S.-K., Ryu, Y., Chang, Y.-T., Whang, D. & Kim, K. (1994). *Carbohydr. Res.* **253**, 13–18.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Falshaw, A., Gainsford, G. J. & Lensink, C. (1999). *Acta Cryst.* **C55**. Submitted.
- Gilbertson, S. R. & Chang, C.-W. T. (1995). *J. Org. Chem.* **60**, 6226–6228.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Latvala, A., Onur, M. A., Gozler, T., Linden, A., Kivcak, B. & Hesse, M. (1995). *Phytochemistry*, **39**, 1229–1240.
- McConnell, J. F., Angyal, S. J. & Stevens, J. D. (1972). *J. Chem. Soc. Perkin Trans.* pp. 2039–2044.
- RajanBabu, T. V., Ayers, T. A. & Casalnuovo, A. L. (1994). *J. Am. Chem. Soc.* **116**, 4101–4102.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
- Siemens (1993). XSCANS. X-ray Single Crystal Analysis System. Version 1.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Spek, A. L. (1998). PLATON98. Molecular Geometry Program. University of Utrecht, The Netherlands.

*Acta Cryst.* (1999). **C55**, 960–962

## N-(Isopropyl)norbornane-endo-2,3-dicarboximide

RYOUKO YOSHIHARA,<sup>a</sup> HIROYUKI HOSOMI,<sup>a</sup> HIROMU AOYAMA<sup>b</sup> AND SHIGERU OHBA<sup>a</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan, and <sup>b</sup>Department of Material Chemistry, Faculty of Textile Science and Technology, Sinsyu University, Tokida 3-15-1, Ueda 386-0081, Japan. E-mail: ohba@chem.keio.ac.jp

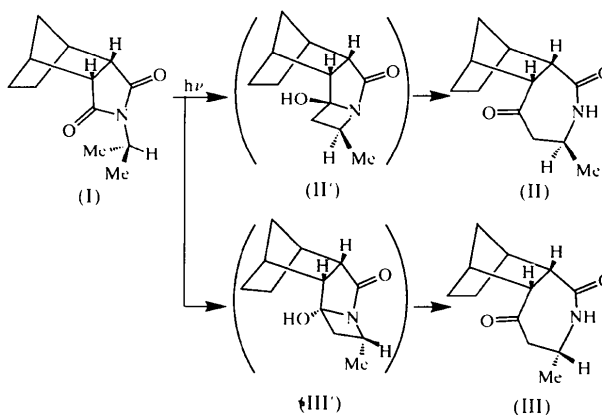
(Received 13 October 1998; accepted 9 February 1999)

## Abstract

The geometry of the title molecule, *N*-isopropylbicyclo[2.2.1]heptane-endo-2,3-dicarboximide, C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>, has been confirmed as the *endo* conformation. The orientation of the isopropyl (<sup>i</sup>Pr) group relative to the succinimide moiety is a little unsymmetric and the <sup>i</sup>Pr group rotates *ca* 6° around the N—C bond from the perpendicular configuration. This causes the stereoselectivity of the photoreaction in the solid state. The diastereomeric excess of the ring expansion products indicates that the carbonyl-O atom predominantly abstracts the nearest  $\gamma$ -hydrogen in the molecule.

## Comment

By photoirradiation of the title compound, (I), the ring expansion products, (II) and (III), were obtained. The reaction may proceed via intramolecular  $\gamma$ -hydrogen abstraction by the carbonyl-O atom to yield the 2-azetidino derivatives, (II') and (III').



When one of the H atoms bonded to C14 in (I) is abstracted by the carbonyl atom O2, compound (II) is obtained. Compound (III) is obtained if an H atom on C15 in (I) is abstracted by O2. In the solid-state reaction

the yield of (II) (38%) is greater than that of (III) (12%). This corresponds well to the molecular geometry in the crystal. The intramolecular O2...C14 distance of 3.214(3) Å is shorter than the O2...C15 distance of 3.370(4) Å. This imbalance is caused by a 6° rotation of the <sup>1</sup>Pr group around the N3—C13 bond axis from the perpendicular configuration, relative to the succinimide moiety.

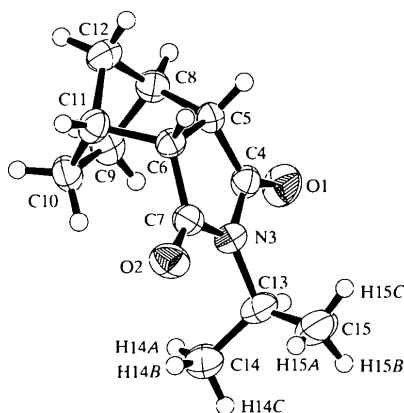


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

The H atoms of the <sup>1</sup>Pr group could not be located on difference syntheses in the present study. Therefore, one of the possible configurations of the propyl H atoms was tentatively assumed. In this model, the nearest  $\gamma$ -hydrogen to atom O2 is H14B (at 2.63 Å), and the second nearest is H15A (at 2.93 Å). The other H atoms bonded to C14 or C15 are 3.58–4.25 Å from O2.

It is interesting that the major product of the photo-reaction of (I) in the acetonitrile solution is (III), which is the minor product in the solid-state reaction. The yields of (II) and (III) in acetonitrile solution were 26 and 40%, respectively.

## Experimental

Compound (I) was synthesized by Diels–Alder addition of *N*-isopropylmaleimide to cyclopentadiene and subsequent hydrogenation of the resulting adduct using palladium on carbon as a catalyst. Crystals of (I) were grown from acetonitrile solution by slow evaporation. The photoreactivity in the solid state was determined by one of the authors (HA). Compound (I) was deposited on the inside wall of a quartz tube as a thin film, by evaporation from methylene chloride solution. Irradiation with a low pressure mercury lamp was performed under argon at 273–283 K. The products were isolated by flash chromatography on silica gel. The two diastereomers, (II) and (III), were assigned on the basis of their <sup>1</sup>H NMR spectra (NOE difference spectra). The ratio of the two products was almost independent of the degree of conversion (20–100%).

## Crystal data

C<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>  
*M<sub>r</sub>* = 207.27  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 6.411(2) Å  
*b* = 20.092(2) Å  
*c* = 8.930(2) Å  
 $\beta$  = 103.24(2)°  
*V* = 1119.7(5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.229 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Cu *K* $\alpha$  radiation  
 $\lambda$  = 1.54184 Å  
 Cell parameters from 25 reflections  
 $\theta$  = 29.4–30.0°  
 $\mu$  = 0.670 mm<sup>-1</sup>  
*T* = 248 K  
 Prism  
 0.6 × 0.6 × 0.5 mm  
 Colourless

## Data collection

Rigaku AFC-7R diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 by integration (Coppens *et al.*, 1965)  
*T<sub>min</sub>* = 0.679, *T<sub>max</sub>* = 0.763  
 2374 measured reflections  
 2186 independent reflections

1978 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.055  
 $\theta_{max}$  = 75°  
*h* = 0 → 8  
*k* = 0 → 25  
*l* = -11 → 11  
 3 standard reflections every 150 reflections  
 intensity decay: none

## Refinement

Refinement on *F*  
*R* = 0.065  
*wR* = 0.151  
*S* = 1.96  
 2186 reflections  
 137 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o) + 0.00504|F_o|^2]$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{max}$  = 0.31 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.31 e Å<sup>-3</sup>  
 Extinction correction:  
 Zachariasen (1967) type 2  
 Gaussian isotropic  
 Extinction coefficient: 0.8 (1)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C4	1.222(3)	N3—C13	1.475(2)
O2—C7	1.213(2)	C13—C14	1.492(4)
N3—C4	1.390(3)	C13—C15	1.461(4)
N3—C7	1.390(3)		
N3—C13—C14	113.0(2)	C14—C13—C15	117.3(2)
N3—C13—C15	113.2(2)		
C7—N3—C13—C14	62.0(3)	C7—N3—C13—C15	-74.3(3)

All H-atom positions were calculated geometrically, with  $U_{iso}(H) = 1.2 U_{eq}(\text{parent atom})$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1232). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

tetracoordinate allyl silanes (Cerveau, 1987), and this reactivity is believed to arise from particularly effective hyperconjugation between the Si—C  $\sigma$ -electrons and the C=C  $\pi$ -system (Fig. 1). Thus, we were interested in investigating whether the hyperconjugation in (I) would lead to any observable structural effects, such as lengthening of the Si—allyl bond, lengthening of the C=C double bond or a decrease in the intrabridgehead N $\cdots$ Si distance, as expected from contributions from the resonance form, (Ia), compared with similar saturated analogues in which hyperconjugation is absent.

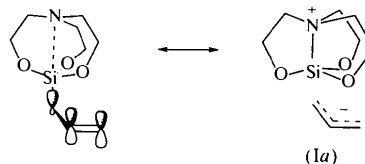


Fig. 1. Hyperconjugation in allylsilatrene.

*Acta Cryst.* (1999). **C55**, 962–963

## Low-temperature structure of allyl silatrane

JONATHAN M. WHITE AND SCOTT JONES

*School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. E-mail: j.white@mail.chemistry.unimelb.edu.au*

(Received 4 June 1998; accepted 5 February 1999)

### Abstract

The structure of the title compound, 1-allyl-2,8,9-trioxo-5-aza-1-silabicyclo[3.3.3]undecane (C<sub>9</sub>H<sub>17</sub>NO<sub>3</sub>Si), was determined in order to study the structural effects which arise from hyperconjugation between the C—Si bond and the allyl double bond. The dative N $\cdots$ Si distance is 2.140 (1) Å.

### Comment

As part of our general interest in the structural consequences of hyperconjugation in silicon compounds (White, 1995), we chose to determine the structure of allyl silatrane, (I). Allyl silatrane has been shown to undergo reaction with electrophiles more readily than

The structure of (I) was determined at 130 K to eliminate the unwanted effects of thermal motion. Although the bicyclic moiety was well ordered, the allyl group was disordered over two positions, with occupancies of 52 (1) and 48 (1)%. This disorder arises from rotation about the C12—C13 bond. Intrabridgehead interaction between the amino group and the Si atom is evidenced by the N5 $\cdots$ Si distance of 2.140 (1) Å, which is considerably shorter than the sum of the van der Waals radii for Si and N (3.65 Å; Bondi, 1964). As a result of this interaction, the Si distorts from a regular tetrahedral geometry towards a trigonal bipyramid, with N5 and C12 at the apical positions and O2, O8 and O9 at the basal positions. This distortion is best exemplified by the bond angles about the Si: the mean O—Si—O angle is 118.7, the mean O—Si—C12 angle is 96.4 and the mean N $\cdots$ Si—O angle is 83.58°.

Owing to the disorder of C13 and C14, the bond distances involving these atoms must be treated as somewhat suspect. Therefore, we cannot make any conclusions regarding structural effects arising from hyperconjugation between the Si—C12 bond and the C13=C14 double bond. However, the Si—C12—C13—C14 torsion angle of 106.8 (3)° is close to the optimum conformation required for this interaction. Consideration of the interatomic distances in the ordered part of the structure of (I) does provide some tentative structural evidence for hyperconjugation between the Si—C12 bond and the allyl  $\pi$ -system. Thus, the N $\cdots$ Si bond of 2.140 (1) Å is slightly shorter than the corresponding distance observed in the analogous structures, (II) [2.173 (2) Å; Hencsei *et al.*, 1988] and (III) [2.177 (4) Å; Hencsei *et al.*, 1989]. Furthermore, the Si—C12 distance of 1.896 (1) Å is slightly longer than the corresponding distances in (II)

