930 reflections
91 parameters
H-atom parameters not refined
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C7	1.249 (3)	N3—C4	1.385 (4)
O2—C7	1.252 (3)	C4—C5	1.346 (4)
N1—C2	1.315 (4)	C4—C6	1.485 (4)
N1—C5	1.373 (4)	C6—C7	1.517 (4)
N3—C2	1.324 (4)		
C2—N1—C5	108.2 (3)	N1—C5—C4	107.9 (3)
C2—N3—C4	108.4 (2)	C4—C6—C7	116.1 (3)
N1—C2—N3	109.3 (3)	O1—C7—O2	125.0 (3)
N3—C4—C5	106.1 (3)	O1—C7—C6	115.7 (3)
N3—C4—C6	123.2 (3)	O2—C7—C6	119.4 (3)
C5—C4—C6	130.7 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.97	1.68	2.639 (3)	173
N3—H3···O3^{ii}	1.05	1.71	2.748 (3)	173
O3—H8···O2^{iii}	1.05	1.76	2.780 (3)	162
O3—H7···O2^{iv}	0.91	1.85	2.752 (3)	168

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

The H atoms of the water molecule were located from difference Fourier maps and the others were generated automatically at ideal positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1019). Services for accessing these data are described at the back of the journal.

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An asatone-type neolignan and its photocage product

Ryouko Yoshihara,[a] Kazuki Mori,[a] Shigeru Nishiyama,[a] Syousuke Yamamura,[a] Hiroyuki Hosomi,[a] Shigeru Ohba[a] and Yoshikatsu Ito[b]

[a]*Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan, and* [b]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan. E-mail: ohba@chem.keio.ac.jp*

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Abstract

The structures of dimethyl 8,8-dimethoxy-7-oxo-1,4-(1,1-dimethoxy-2-oxoethano)-1,4,4a,7,8,8a-hexahydronaphthalene-2,4a-diyldiacrylate, $C_{24}H_{28}O_{10}$, (I), and its photocage product, dimethyl 6,6,12,12-tetramethoxy-5,11-dioxotetracyclo[6.2.2.0^{3,10}.0^{4,9}]dodecane-2,9-diyldiacrylate, $C_{24}H_{28}O_{10}$, (II), were determined in order to investigate the conformational change caused by the intramolecular [2+2] photoreaction. The high efficiency (70%) of the photoreaction of (I) in a 1,4-dioxane solution is attributed to the fact that two C═C double bonds in (I) can become close and parallel to each other simply by changing the configuration of the cyclohexene ring moiety from an envelope to a sofa form. Compound (I) is much less photoreactive in the solid state than in solution.

Comment

The isolation and characterization of asatone, isoasatone and related neolignans have been reported previously by Sasaki *et al.* (1973) and Yamamura *et al.* (1976), and the synthesis of asatone by anodic oxidation has been reported by Nishiyama *et al.* (1983). The asatone-type compound (I) could be transformed efficiently to the isoasatone-type cage compound (II) by photoirradiation in solution. The photoreactivity of (I) in the solid state has also been examined, showing that it is much less

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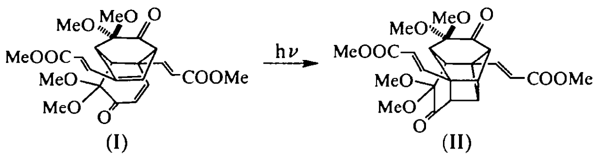
reactive than in solution. The yield of (II) was 15% when powder crystals of (I) were irradiated with UV light from a mercury lamp for 25 h under argon at room temperature, compared with a 70% yield when irradiated for 30 min in a dioxane solution.



In (I), there are two independent molecules and their structures are essentially identical except for the orientations of the methylacrylate groups. The intramolecular distances between the C atoms which participate in the photoreaction are C15···C27 2.878 (2), C16···C26 3.537 (2), C15*···C27* 2.822 (3) and C16*···C26* 3.510 (2) Å. In (II), the bond distances after photoreaction are C15—C27 1.554 (3) and C16—C26 1.593 (3) Å. Comparing the molecular structures of (I) and (II), the carbon skeleton of the fused-ring system is almost unchanged except for the positions of atoms C15 and C16. The configuration of the C11–C16 six-membered ring is an envelope in (I), with atom C12 at the apex. In (II), this ring has a sofa form, where the boundary of the sofa is the C13···C16 line. The C11—C16—C15—C14 torsion angle is 5.4 (3)° in the first of the two molecules of (I), 4.2 (3)° in the second of the two molecules of (I) and 48.6 (3)° in (II).

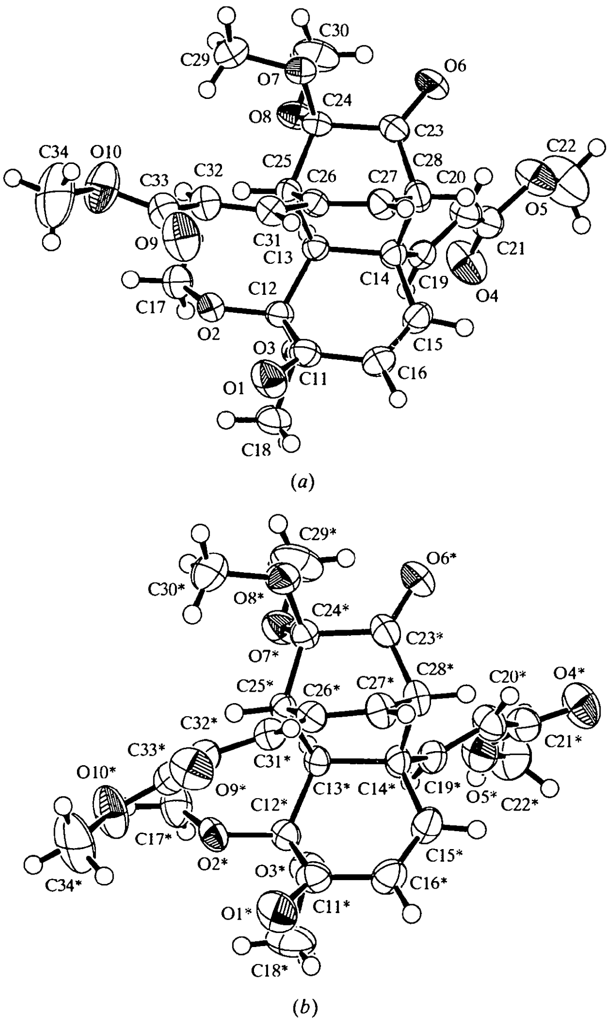


Fig. 1. The molecular structures of the two independent molecules of (I) shown in (*a*) and (*b*). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

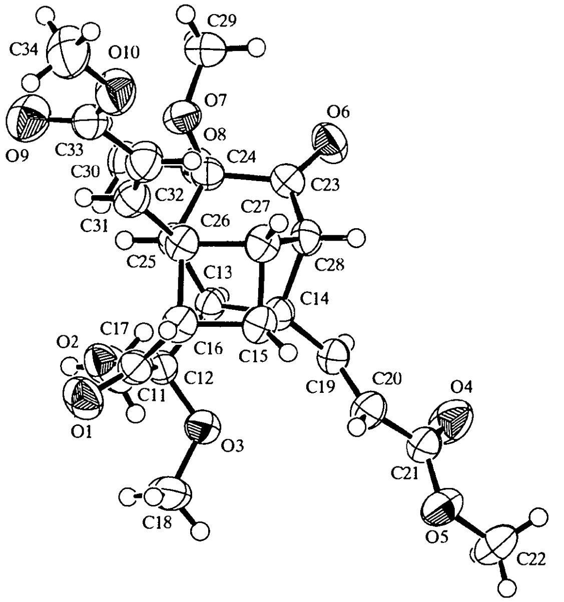


Fig. 2. The molecular structure of (II). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

In the October 1998 release of the CSD (Cambridge Structural Database, 1998), there are 11 entries of asatone-type compounds similar to (I), but only three of isoasatone-type cage compounds similar to (II) (Becker *et al.*, 1981; Jones & Karle, 1974; Sasaki & Hirata, 1974).

Experimental

To a solution of methyl *trans*-ferulate (104 mg) in methanol (140 ml) was added $LiClO_4$ as a supporting salt. Constant-current electrolysis under argon was carried out for 3.5 h using a Pt wire as the cathode and a glassy carbon beaker as the anode. The mechanism of anodic oxidation seems to be phenol-oxidative methoxylation and dimerization by the Diels–Alder reaction (Nishiyama *et al.*, 1983). The product, (I), was purified by preparative thin-layer chromatography (PTLC) (yield 74%; m.p. 436 K). A solution of (I) (80 mg) in 1,4-dioxane (300 ml) was irradiated with a high-pressure mercury lamp at 273 K for 35 min. The photoproduct, (II), was purified by PTLC (yield 70%; m.p. 461 K). The estimation of the yield was based on NMR spectra. Crystals of (I) and (II) were grown by slow evaporation from methanol and 1,4-dioxane solutions, respectively.

Compound (I)

Crystal data

$C_{24}H_{28}O_{10}$
$M_r = 476.48$
Triclinic
$P\overline{1}$
$a = 16.014\ (2)$ Å
$b = 16.097\ (1)$ Å
$c = 9.7547\ (7)$ Å
$\alpha = 95.827\ (6)^\circ$
$\beta = 104.757\ (7)^\circ$
$\gamma = 84.810\ (8)^\circ$
$V = 2413.6\ (4)$ Å^3
$Z = 4$
$D_x = 1.311$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 29.6$–30.0°
$\mu = 0.867$ mm^{-1}
$T = 248$ K
Prismatic
0.45 × 0.30 × 0.30 mm
Colourless

Data collection

Rigaku AFC-7*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min} = 0.717$, $T_{\max} = 0.814$
9688 measured reflections
9330 independent reflections
8150 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.007$
$\theta_{\max} = 75^\circ$
$h = 0 \rightarrow 20$
$k = -20 \rightarrow 20$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: 3.6%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.102$
$S = 1.62$
9330 reflections
637 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.00297|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths and torsion angles (Å, °) for the two independent molecules of (I)*

C11—C12	1.546 (2)	C15—C16	1.320 (3)
C11—C16	1.474 (2)	C15*—C16*	1.323 (3)
C11*—C12*	1.536 (2)	C23—C24	1.552 (2)
C11*—C16*	1.454 (3)	C23—C28	1.515 (2)
C12—C13	1.532 (2)	C23*—C24*	1.553 (2)
C12*—C13*	1.534 (2)	C23*—C28*	1.512 (2)
C13—C14	1.566 (2)	C24—C25	1.543 (2)
C13—C25	1.551 (2)	C24*—C25*	1.547 (2)
C13*—C14*	1.563 (2)	C25—C26	1.516 (2)
C13*—C25*	1.546 (2)	C25*—C26*	1.513 (2)
C14—C15	1.519 (2)	C26—C27	1.343 (2)
C14—C28	1.574 (2)	C26*—C27*	1.343 (2)
C14*—C15*	1.507 (2)	C27—C28	1.513 (2)
C14*—C28*	1.574 (2)	C27*—C28*	1.514 (2)
C11—C12—C13—C14	46.7 (2)		
C11—C16—C15—C14	5.4 (3)		
C11*—C12*—C13*—C14*	46.9 (2)		
C11*—C16*—C15*—C14*	4.2 (3)		
C12—C11—C16—C15	26.7 (2)		
C12—C13—C14—C15	−17.0 (2)		
C12*—C11*—C16*—C15*	22.9 (3)		
C12*—C13*—C14*—C15*	−21.9 (2)		
C13—C12—C11—C16	−52.5 (2)		
C13—C14—C15—C16	−10.4 (2)		
C13*—C12*—C11*—C16*	−48.3 (2)		
C13*—C14*—C15*—C16*	−4.5 (3)		

Compound (II)

Crystal data

$C_{24}H_{28}O_{10}$
$M_r = 476.48$
Monoclinic
$P2_1/n$
$a = 15.356\ (3)$ Å
$b = 8.659\ (3)$ Å
$c = 17.271\ (4)$ Å
$\beta = 94.31\ (2)^\circ$
$V = 2289.8\ (9)$ Å^3
$Z = 4$
$D_x = 1.382$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 29.3$–30.0°
$\mu = 0.914$ mm^{-1}
$T = 248$ K
Plate-like
0.6 × 0.5 × 0.2 mm
Colourless

Data collection

Rigaku *AFC*-7*R* diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min} = 0.602$, $T_{\max} = 0.848$
4619 measured reflections
4465 independent reflections
3772 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.040$
$\theta_{\max} = 75^\circ$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 21$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.063$
$wR = 0.122$
$S = 1.571$
4465 reflections
307 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.00449|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C11—C12	1.546 (3)	C15—C27	1.554 (3)
C11—C16	1.483 (3)	C16—C26	1.593 (3)
C12—C13	1.542 (3)	C23—C24	1.547 (3)
C13—C14	1.551 (3)	C23—C28	1.502 (3)
C13—C25	1.531 (3)	C24—C25	1.545 (3)
C14—C15	1.570 (3)	C25—C26	1.546 (3)
C14—C28	1.590 (3)	C26—C27	1.574 (3)
C15—C16	1.546 (3)	C27—C28	1.532 (3)
C15—C14—C28	88.8 (1)	C16—C26—C27	88.7 (2)
C14—C15—C27	86.4 (2)	C15—C27—C26	86.8 (2)
C16—C15—C27	91.2 (2)	C15—C27—C28	91.6 (2)
C15—C16—C26	86.4 (2)	C14—C28—C27	86.4 (1)

C11—C12—C13—C14	68.7 (2)	C12—C13—C14—C15	−57.6 (2)
C11—C16—C15—C14	48.6 (3)	C13—C12—C11—C16	−18.6 (2)
C12—C11—C16—C15	−38.4 (3)	C13—C14—C15—C16	0.9 (2)

All H-atom positions were calculated geometrically, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent atom). Refinements were based on all the independent reflections. The threshold $I > 2\sigma(I)$ was used only for calculation of the R factor. In (I), there is an orientational disorder of a methylacrylate moiety in one of the two independent molecules; this disorder is similar to that observed in (*E*)-stilbenes and other related compounds (Harada *et al.*, 1997). The central C═C double bond has two possible orientations which are approximately perpendicular to each other, and the terminal COOMe moiety is only a little rotated in its plane. The site-occupancy factors of these two possible sets of positions, C19═C20—C21(═O4)—O5—C22 and C119═C120—C121(═O104)—O105—C122, were assumed to be 80 and 20%, respectively, and the atoms in the minor part were refined isotropically. H atoms were not introduced for the minor part.

For both compounds, 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 structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1086). Services for accessing these data are described at the back of the journal.

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Diisopropylammonium diphenylmethylnitronate at 200 K

Mark Sievert, Norbert Nagel, Hans Bock* and Rüdiger Dienelt

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Straße 11, 60439 Frankfurt/Main, Germany. E-mail: nagel@chemie.uni-frankfurt.de

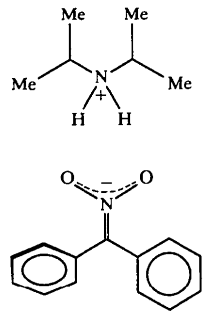
(*Received 17 September 1998; accepted 22 February 1999*)

Abstract

In the crystal structure of the title compound, $C_6H_{16}N^+\cdot C_{13}H_{10}NO_2^-$, the ions are arranged in quadruples, in which two cations and two anions form a cyclic hydrogen-bonded system.

Comment

The structure of diisopropylammonium diphenylmethylnitronate, (I), is of particular interest owing to the formation of a 12-membered macrocycle containing four polar hydrogen-bond bridges N—H···O, which due to their cooperative effect provide an example of molecular self-organization. Crystals are obtained as colourless prisms from the reaction mixture of *aci*-nitrodiphenylmethane (Colvin *et al.*, 1980; Konowalow, 1896) with diisopropylamine at 258 K. Sets of two symmetry-equivalent protonated molecular cations and two equivalent anions form hydrogen-bonded molecular-ion quadruples within undulating layers parallel to the *xy* plane (Fig. 1). The packing is supported by additional weak C—H···π



(I)