(fixed at $B = 5{\cdot}0$ Å²). $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1{\cdot}0$ for $F_o < 598{\cdot}5$, $w = (598{\cdot}5/F_o)^2$ for $F_o \geq 598{\cdot}5$. Final $R = 0{\cdot}036$, $wR = 0{\cdot}034$, $S = 2{\cdot}98$ for 451 variables, secondary-extinction factor (g) 6·27 (7) $\times 10^{-7}$ [$|F_o| = |F_c|/(1 + gIc)$]; $\Delta/\sigma < 0{\cdot}25$, largest peak in final ΔF map $+0{\cdot}40$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs: Enraf–Nonius *SDP* (Frenz, 1984), *ORTEP*II (Johnson, 1976). The structure of CAM is shown in Fig. 1, a packing diagram in Fig. 2; positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1, bond distances and angles in Table 2.*

Related literature. Title compound has antitumor and immunosuppressive activity (Ohsugi, Suzuki & Takagi, 1976). For the preparation see Mori, Takaku & Suzuki (1983).

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* Lists of structure factors, anisotropic thermal parameters, torsion angles, least-squares planes and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44328 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1988). C**44**, 198–200

1,2-Dihydro-5,6-dimethoxy-1-benzocyclobutenyl 3,5-Dinitrobenzoate

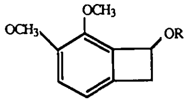
By Upali Siriwardane, R. Thimma Reddy, Shirley S. C. Chu* and Edward R. Biehl

Departments of Chemistry and Electrical Engineering, Southern Methodist University, Dallas, Texas 75275, *USA*

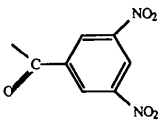
(*Received* 23 *June* 1987; *accepted* 3 *September* 1987)

Abstract. $C_{17}H_{14}N_2O_8$, $M_r = 374{\cdot}31$, monoclinic, $P2_1/n$, $a = 10{\cdot}371$ (3), $b = 22{\cdot}759$ (6), $c = 7{\cdot}442$ (2) Å, $\beta = 106{\cdot}62$ (2)°, $V = 1683{\cdot}2$ (7) Å³, $Z = 4$, $D_x = 1{\cdot}48$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}76$ cm^{-1}, $F(000) = 776$, $T = 295$ K. Final $R = 0{\cdot}038$ for 1481 observed reflections. The cyclobutene ring is nearly planar. The bond distances are C=C(cyclobutene) = 1·386 (4), C—C(cyclobutene, av.) = 1·542 (4), C—O(benzo, av.) = 1·362 (4), C—O(cyclobutene) = 1·445 (3), C—C(benzo, av.) = 1·384 (4) and O—CH_3(av.) = 1·432 (4) Å. The X-ray structure confirms benzocyclobutenimine as an intermediate in a re-arrangement reaction.

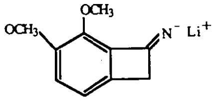
Experimental. The title compound (I) was prepared as a dinitrobenzoate derivative of (II) to obtain X-ray-quality single crystals. Recently, we have found a novel tandem-addition rearrangement *via* a benzocyclobutenimine intermediate (III) leading to the parent alcohol (II) which was isolated in 25% yield as a fluffy white crystalline material by the reaction of lithioacetonitrile with 3,4-dimethoxy-1,3-cyclohexadien-5-yne (generated *in situ* with lithiodiisopropylamine in THF) followed by aqueous work-up.



(I) : R =



(II) : R= H



(III)

Unit-cell parameters by least-squares fit of 15 reflections in the range $10 < 2\theta < 25°$, crystal dimensions $0{\cdot}64 \times 0{\cdot}45 \times 0{\cdot}18$ mm, space group $P2_1/n$ from systematic absences ($0k0$, k odd; $h0l$, $h + l$ odd); automatic Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, variable scan rate (3·0–14·7° min^{-1}, depending on intensity), 2571 measured reflections, 2208 independent reflections in the range $3 < 2\theta < 45°$, $R_{\text{int}} = 0{\cdot}008$, hkl range h 10→−11, k 0→23, l 0→8, 1481 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics;

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* To whom correspondence should be addressed.

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three standard reflections remeasured after every 100 reflections did not show any significant change (~4%) in intensity during data collection; Lorentz–polarization correction, no absorption or extinction corrections. Direct methods *SHELXS*86 (Sheldrick, 1986), refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), anisotropic; H atoms located in difference Fourier maps, H atoms isotropic; $w = 1/(\sigma^2F + 0{\cdot}000091F^2)$, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}038$, $wR = 0{\cdot}037$ for 1481 observed reflections; $S = 2{\cdot}04$, $(\Delta/\sigma)_{\max} = 0{\cdot}12$, $\Delta\rho_{\max,\min} = 0{\cdot}11$, $-0{\cdot}13\ \text{e Å}^{-3}$ in final difference Fourier map. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,* selected bond lengths, angles and torsion angles are given in Table 2. The identification of the atoms and the configuration are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1; the packing of the molecules is shown in the unit cell in Fig. 2.

Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-*H *atoms (e.s.d.'s in parentheses)*

	x	y	z	U_{eq}*(Å^2)
O(1)	0·0233 (2)	0·73248 (7)	0·1869 (2)	0·0550 (4)
O(2)	−0·3409 (2)	0·72069 (7)	0·1919 (3)	0·0694 (5)
O(3)	−0·5033 (2)	0·63968 (8)	0·0211 (3)	0·0710 (5)
O(4)	0·2422 (2)	0·72325 (8)	0·3412 (3)	0·0625 (5)
O(5)	−0·1424 (2)	0·91447 (9)	−0·1274 (4)	0·1033 (8)
O(6)	−0·0050 (2)	0·97667 (8)	−0·1885 (3)	0·0724 (5)
O(7)	0·4594 (2)	0·96469 (10)	0·1574 (4)	0·1131 (8)
O(8)	0·5432 (2)	0·88131 (10)	0·2564 (4)	0·1008 (8)
C(1)	−0·0063 (3)	0·68107 (11)	0·2821 (4)	0·0555 (7)
C(2)	−0·1474 (3)	0·65861 (10)	0·1933 (4)	0·0477 (7)
C(3)	−0·2822 (3)	0·67083 (10)	0·1538 (4)	0·0500 (7)
C(4)	−0·3698 (2)	0·62578 (11)	0·0621 (4)	0·0514 (7)
C(5)	−0·3216 (3)	0·57255 (11)	0·0210 (4)	0·0547 (7)
C(6)	−0·1851 (3)	0·56014 (12)	0·0674 (4)	0·0638 (8)
C(7)	−0·1007 (3)	0·60473 (11)	0·1518 (4)	0·0553 (7)
C(8)	0·0457 (3)	0·62167 (12)	0·2287 (4)	0·0698 (8)
C(9)	0·1516 (2)	0·75063 (11)	0·2393 (4)	0·0502 (6)
C(10)	0·1685 (2)	0·80883 (10)	0·1594 (3)	0·0440 (6)
C(11)	0·0595 (2)	0·84058 (11)	0·0503 (4)	0·0481 (6)
C(12)	0·0838 (3)	0·89590 (11)	−0·0080 (4)	0·0486 (6)
C(13)	0·2100 (2)	0·92108 (11)	0·0344 (4)	0·0530 (7)
C(14)	0·3136 (2)	0·88736 (12)	0·1390 (4)	0·0518 (7)
C(15)	0·2966 (2)	0·83225 (11)	0·2032 (4)	0·0485 (6)
C(16)	−0·2514 (3)	0·76632 (12)	0·2853 (5)	0·0741 (9)
C(17)	−0·5985 (3)	0·59850 (12)	−0·0869 (5)	0·0702 (9)
N(1)	−0·0306 (2)	0·93148 (9)	−0·1171 (3)	0·0629 (6)
N(2)	0·4493 (2)	0·91305 (10)	0·1877 (4)	0·0721 (6)

* The standard deviations of U_{eq}'s were calculated according to Schomaker & Marsh (1983).

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

O(1)—C(1)	1·445 (3)	O(4)—C(9)	1·200 (3)
O(1)—C(9)	1·340 (3)	C(1)—C(2)	1·512 (4)
O(2)—C(3)	1·356 (4)	C(1)—C(8)	1·549 (4)
O(2)—C(16)	1·433 (4)	C(2)—C(7)	1·386 (4)
O(3)—C(4)	1·367 (3)	C(7)—C(8)	1·512 (4)
O(3)—C(17)	1·430 (4)	C(9)—C(10)	1·483 (3)
C(1)—O(1)—C(9)	116·0 (2)	C(2)—C(7)—C(8)	93·8 (2)
O(1)—C(1)—C(2)	112·0 (2)	C(6)—C(7)—C(8)	143·5 (3)
O(1)—C(1)—C(8)	116·3 (2)	C(1)—C(8)—C(7)	86·3 (2)
C(2)—C(1)—C(8)	87·5 (2)	O(1)—C(9)—C(4)	123·9 (2)
C(1)—C(2)—C(3)	145·5 (3)	O(1)—C(9)—C(10)	112·3 (2)
C(1)—C(2)—C(7)	92·3 (2)		
O(1)—C(1)—C(2)—C(3)	−63·9 (5)	C(2)—C(1)—O(1)—C(9)	−171·1 (2)
O(1)—C(1)—C(2)—C(7)	119·4 (2)	C(3)—C(4)—O(3)—C(17)	174·5 (2)
O(1)—C(1)—C(8)—C(7)	−115·2 (2)	C(8)—C(1)—O(1)—C(9)	−72·6 (3)
C(1)—O(1)—C(9)—O(4)	8·9 (4)	C(2)—C(3)—O(2)—C(16)	−0·2 (4)
C(1)—O(1)—C(9)—C(10)	−170·2 (2)		

Related literature. Compounds (I) and (II) are representatives of a class of compound known as cyclobutenols which undergo intra- or intermolecular condensations with dienophiles to give rise to a wide variety of biological compounds such as quinones, steroids, alkaloids and lignins (Oppolzer, 1978).

This work was supported by the Robert A. Welch foundation under grants N-495 (SSCC) and N-118 (ERB).

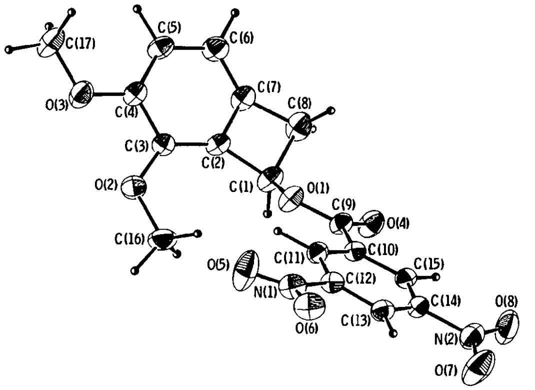

Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids are scaled to enclose 30% probability. H atoms are represented as spheres of arbitrary radii.

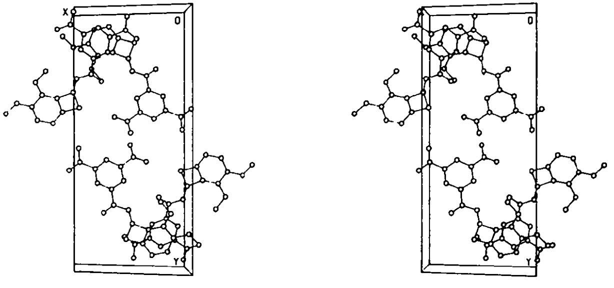

Fig. 2. Stereoscopic drawing showing the packing of molecules in the unit cell. H atoms are removed for clarity.

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* Anisotropic temperature factors, bond lengths, bond angles, torsion angles, hydrogen parameters, least-squares-plane data and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44337 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1988). C**44**, 200–201

6-(3-Methoxybenzyl)-5-methyl-*o*-anisonitrile

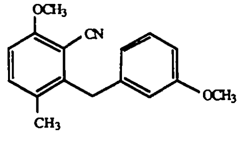
BY UPALI SIRIWARDANE, SUBHASH P. KHANAPURE, SHIRLEY S. C. CHU* AND EDWARD R. BIEHL

Departments of Chemistry and Electrical Engineering, Southern Methodist University, Dallas, Texas 75275, *USA*

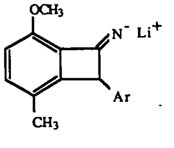
(*Received* 23 *June* 1987; *accepted* 3 *September* 1987)

Abstract. $C_{17}H_{17}NO_2$, $M_r = 267{\cdot}33$, monoclinic, $P2_1/c$, $a = 7{\cdot}038\,(2)$, $b = 26{\cdot}372\,(6)$, $c = 7{\cdot}779\,(2)$ Å, $\beta = 100{\cdot}93\,(2)°$, $V = 1428{\cdot}5\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}76$ cm^{-1}, $F(000) = 568$, $T = 295$ K. Final $R = 0{\cdot}051$ for 1275 observed reflections. The bond distances are H_2C—C(av.) = 1·509 (4), C≡N = 1·135 (4), C—CH_3 = 1·444 (4), C—O(av.) = 1·360 (4) and C—C(benz., av.) = 1·383 (4) Å. The X-ray structure confirms regioselective addition to the 1 position of the 1,3-cyclohexadien-5-yne.

Experimental. Recently, we have observed a novel tandem-addition rearrangement *via* a benzocyclobutenimine intermediate (II) leading to contiguously substituted benzenes such as the title compound (I), which was obtained as an unexpected product in 49% yield by the reaction of 3-methoxylithioarylonitrile with 1-methoxy-4-methyl-1,3-cyclohexadien-5-yne (generated *in situ* with lithiodiisopropylamine in THF) followed by protonation.



(I)



(II)

Crystals of (I) are colorless rectangular plates, unit-cell parameters by least-squares fit of 15 reflections in the range $10 < 2\theta < 25°$, crystal dimensions 0·34 × 0·16 × 0·35 mm, space group $P2_1/c$ from systematic absences (0*k*0, *k* odd; *h*0*l*, *h*+*l* odd); automatic Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, variable scan rate (3·0–14·7° min^{-1}, depending on intensity), 2195 measured reflections, 1887 independent reflections in the range $3 < 2\theta < 45°$, $R_{\rm int} = 0{\cdot}017$, *hkl* range h −7→7, k 0→28, l 0→8, 1275 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; three standard reflections remeasured after every 100 reflections did not show any significant change (~3%) in intensity during data collection; Lorentz–polarization correction, no absorption or extinction corrections. Direct methods *SHELXS86* (Sheldrick, 1986), refinement by full-matrix least squares using *SHELX76* (Sheldrick, 1976), anisotropic; H atoms located in difference Fourier maps, H atoms included in the refinement with isotropic temperature factors and with the constraint as benzyl, methyl and —CH_2—; $w = 1/(\sigma^2F + 0{\cdot}003988F^2)$, $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}051$ and $wR = 0{\cdot}060$ for 1275 observed reflections; $S = 1{\cdot}12$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}03$, $\Delta\rho_{\rm max,\,min} = 0{\cdot}31$, $-0{\cdot}18$ e Å^{-3} in final difference Fourier map. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,† selected bond lengths, angles and torsion angles are given in Table 2. The identification of the atoms and the configuration are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1, the packing of the molecules is shown in the unit cell in Fig. 2.

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* To whom correspondence should be addressed.

† Anisotropic temperature factors, bond lengths, bond angles, torsion angles, hydrogen parameters and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44336 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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