Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: none
3646 measured reflections
1768 independent reflections
1658 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0657$
$\theta_{\max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 22$
3 standard reflections monitored every 200 reflections frequency: 57 min intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0577$
$wR(F^2) = 0.1502$
$S = 1.073$
1766 reflections
149 parameters
H atoms refined freely with individual isotropic displacement parameters
$w = 1/[\sigma^2(F_o^2) + (0.103P)^2 + 0.0579P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.73$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ 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)*

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

	x	y	z	$U_{\rm eq}$
O4	0.1598 (3)	0.6195 (2)	0.21944 (9)	0.0166 (7)
O3	0.5273 (3)	0.3655 (2)	0.23980 (9)	0.0178 (8)
O2	0.2836 (3)	0.1363 (2)	0.34049 (9)	0.0168 (8)
O5	0.0064 (3)	0.4114 (2)	0.40628 (8)	0.0205 (8)
O1	0.3464 (3)	0.5074 (2)	0.46638 (9)	0.0254 (11)
C4	0.1539 (3)	0.4858 (2)	0.27680 (11)	0.0129 (9)
C3	0.3939 (3)	0.4331 (3)	0.30305 (11)	0.0135 (9)
C5	0.0163 (4)	0.5445 (3)	0.34791 (12)	0.0186 (10)
C1	0.2291 (4)	0.3661 (3)	0.43439 (12)	0.0199 (11)
C2	0.3775 (4)	0.2969 (2)	0.36760 (11)	0.0153 (9)
C6	0.2401 (7)	0.5725 (4)	0.5364 (2)	0.037 (2)

Table 2. *Selected torsion angles (°) and hydrogen-bonding parameters (Å, °)*

C1—O5—C5—C4	61.16	C1—C2—C3—C4	−55.25
O5—C1—C2—C3	57.66	C3—C4—C5—O5	−57.08

D—H···A	D—H	H···A	D···A	D—H···A
O2—H22···O5	0.83 (3)	2.50 (3)	2.890 (2)	110 (3)
O2—H22···O4$^{\rm i}$	0.83 (3)	1.99 (3)	2.773 (3)	157 (3)
O3—H23···O2$^{\rm ii}$	0.86 (3)	1.88 (2)	2.729 (2)	173 (3)
O4—H24···O3$^{\rm ii}$	0.84 (2)	1.88 (3)	2.718 (2)	178 (3)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Strained Cyclononadienyne

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Abstract

The title compound, methyl 8-chlorobicyclo[7.1.0]-deca-1,8-dien-4-yne-2-carboxylate, $C_{12}H_{11}ClO_2$, crystallizes with two chemically equivalent and essentially geometrically and conformationally identical molecules in the asymmetric unit. A cyclopropane ring is fused to a nine-membered ring such that it is flanked by two double bonds; the presence of a triple bond in the larger ring generates considerable strain, evidenced in the marked non-linearity of the alkyne unit [165.2 (2)–168.4 (2)° at the C atoms] and the wide angles within the nine-membered ring at the ring fusion atoms [153.09 (10)–155.5 (2)°].

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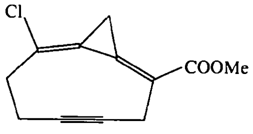
Comment

As part of a study of vinylcyclopropenes, the title compound, (I), was isolated as the product of trapping lithiocyclopropene with methyl chloroformate in a 2:1 stoichiometry (Al Dulayymi & Baird, 1996). The identity of the compound was established by ^1H and ^{13}C NMR spectroscopy but, since both the product and the proposed mechanism of its formation are very unusual, we have confirmed it crystallographically.



(I)

The asymmetric unit of the crystal structure consists of two molecules (Fig. 1), which are chemically identical and have essentially the same internal geometry and conformation (Table 2), but different and crystallographically unrelated orientations. The molecules shown in Fig. 1 correspond to the coordinates of Table 1 and are actually enantiomers of each other which accounts for the difference in appearance around C5, C6, C17 and C18; a least-squares fit indicates a very close match of one molecule to the inverse of the other. For both molecules, eight of the atoms of the nine-membered ring are approximately coplanar: r.m.s. deviations are 0.071 Å for the first ring excluding C5, and 0.061 Å for the second ring excluding C17. The dihedral angle between these two mean planes is 36.30 (3)°. As viewed in Fig. 1, C5 lies 0.651 (2) Å above the plane of the first ring and C2 lies 0.292 (2) Å below it; C17 lies 0.633 (2) Å below the plane of the second ring and C14 lies 0.265 (2) Å above it. The centroids of the two molecules are separated approximately by the vector [0.5, 0, 0]. There are no notably short intermolecular contacts.

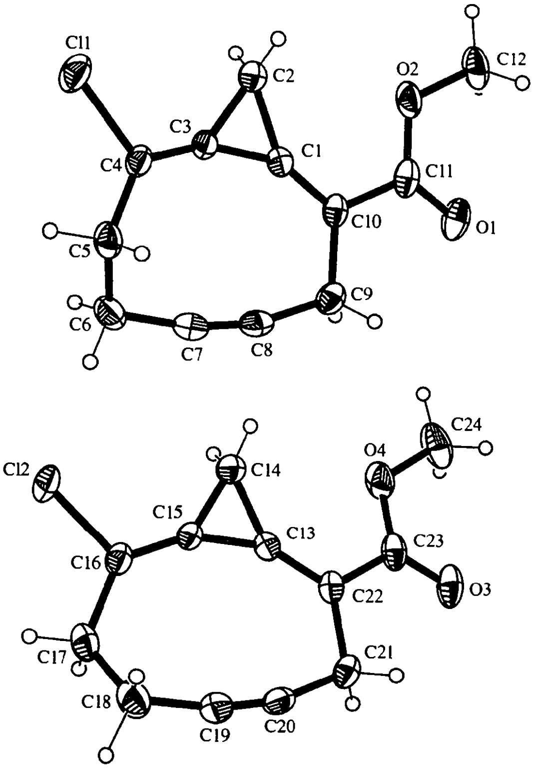


Fig. 1. A view of both molecules in their correct relative positions, with atom labels and 50% probability ellipsoids for non-H atoms. H atoms are represented by small circles of arbitrary radius.

The bicyclic core of the each molecule has several ingredients of severe strain, with one triple bond and with a cyclopropane ring flanked by two double bonds. The strain is particularly marked in the large deviation of the alkyne unit from linearity and in the angles at ring junction atoms, and hardly affects the CH_2 links in the nine-membered ring.

Deviations of more than 10° from linearity for alkyne units are very rare in structures free of disorder (which may produce apparent non-linearity as an artefact) and not involving metal coordination. They are mostly found in rings of six–eight atoms; structures of 10 such compounds are contained in the April 1996 release of the Cambridge Structural Database (Allen & Kennard, 1993), half of them having several Si atoms in the ring: these atoms can more easily accommodate a wide range of bond angles than can C atoms.

Although there are many bismethylenecyclopropanes and radialenes (trismethylenecyclopropanes) known [for example, the parent bismethylenecyclopropane itself (Bloch, Le Perchec & Conia, 1970) and a bicyclo derivative (Belzner & Szeimies, 1986)], crystallographic characterization of a cyclopropane ring flanked by two double bonds is rare other than the special case of the hexacyanotrimethylenecyclopropanide anion which has three radial double bonds (11 compounds with this anion are in the Cambridge Structural Database, together with two related compounds). Otherwise the database contains only examples with a metal-coordinated cyclopropanaphthalene ligand (Muller, Bernardinelli & Jacquier, 1988) and a series of oxidized porphyrinato metal complexes (De Angelis, Solari, Floriani, Chiesi-Villa & Rizzoli, 1994) but no purely organic molecule.

There appears to be only one other published example of a cyclonona-1,3-dien-6-yne in which the two adjacent CH_2 groups form a ring fusion with a cyclopentane ring (Meier, Hanold, Molz, Bissinger, Kolshorn & Zountsas, 1986) and this has not been characterized crystallographically.

Experimental

Compound (I) was obtained as the product of trapping of a lithiocyclopropene with methyl chloroformate and has been characterized by NMR spectroscopy (Al Dulayymi & Baird, 1996). It was recrystallized from diethyl ether/petrol (313–333 K boiling range) by vapour diffusion.

Crystal data

$C_{12}H_{11}ClO_2$
$M_r = 222.66$
Monoclinic
$P2_1/c$
$a = 14.8887\,(10)$ Å
$b = 20.4239\,(13)$ Å
$c = 7.1847\,(5)$ Å
$\beta = 100.743\,(2)°$
$V = 2146.5\,(2)$ Å^3
$Z = 8$
$D_x = 1.378$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6551 reflections
$\theta = 2.78–28.31°$
$\mu = 0.331$ mm^{-1}
$T = 160\,(2)$ K
Plate
$0.40 \times 0.40 \times 0.02$ mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: none
13439 measured reflections
4994 independent reflections

3362 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0369$
$\theta_{\rm max} = 28.55°$
$h = -19 \rightarrow 19$
$k = -27 \rightarrow 26$
$l = -9 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0454$
$wR(F^2) = 0.1133$
$S = 1.020$
4994 reflections
274 parameters
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.58P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.50$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0010 (4)
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)*

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

	x	y	z	$U_{\rm eq}$
C1	0.41091 (13)	0.72031 (9)	0.2310 (3)	0.0231 (4)
C2	0.31691 (14)	0.69465 (9)	0.2244 (3)	0.0282 (5)
C3	0.39813 (13)	0.65093 (9)	0.2323 (3)	0.0235 (4)
C4	0.42456 (14)	0.58904 (9)	0.2594 (3)	0.0252 (4)
C5	0.51750 (14)	0.55750 (10)	0.3038 (3)	0.0302 (5)
C6	0.58421 (15)	0.57786 (11)	0.1765 (3)	0.0339 (5)
C7	0.59723 (14)	0.64884 (11)	0.1856 (3)	0.0310 (5)
C8	0.59215 (14)	0.70665 (11)	0.1991 (3)	0.0297 (5)
C9	0.56111 (14)	0.77416 (10)	0.2103 (3)	0.0292 (5)
C10	0.46133 (14)	0.77389 (9)	0.2264 (3)	0.0244 (4)
C11	0.42039 (15)	0.84037 (10)	0.2342 (3)	0.0281 (5)
C12	0.28951 (17)	0.90193 (10)	0.2562 (3)	0.0400 (6)
O1	0.46356 (11)	0.89009 (7)	0.2308 (2)	0.0384 (4)
O2	0.33185 (10)	0.83865 (7)	0.2463 (2)	0.0336 (4)
Cl1	0.33526 (4)	0.53249 (2)	0.26229 (8)	0.03676 (16)
C13	0.91919 (13)	0.71978 (9)	0.2029 (3)	0.0229 (4)
C14	0.82487 (14)	0.69550 (10)	0.1330 (3)	0.0300 (5)
C15	0.90493 (13)	0.65084 (9)	0.1890 (3)	0.0233 (4)
C16	0.92982 (14)	0.58863 (10)	0.1846 (3)	0.0264 (4)
C17	1.02217 (16)	0.55677 (10)	0.2110 (3)	0.0362 (5)
C18	1.08988 (16)	0.57578 (11)	0.3867 (3)	0.0389 (6)
C19	1.10377 (15)	0.64712 (11)	0.3923 (3)	0.0328 (5)
C20	1.09956 (14)	0.70510 (11)	0.3790 (3)	0.0279 (5)
C21	1.06957 (14)	0.77291 (10)	0.3435 (3)	0.0279 (5)
C22	0.96978 (14)	0.77325 (9)	0.2495 (3)	0.0235 (4)
C23	0.92903 (16)	0.83945 (10)	0.2114 (3)	0.0284 (5)
C24	0.7954 (2)	0.90050 (11)	0.0995 (4)	0.0484 (7)
O3	0.97250 (12)	0.88944 (7)	0.2437 (2)	0.0396 (4)
O4	0.83958 (11)	0.83762 (7)	0.1376 (2)	0.0369 (4)
Cl2	0.83931 (4)	0.53314 (3)	0.11172 (8)	0.03696 (16)

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

C1—C10	1.331 (3)	C13—C22	1.333 (3)
C1—C3	1.430 (3)	C13—C15	1.425 (3)
C1—C2	1.487 (3)	C13—C14	1.486 (3)
C2—C3	1.496 (3)	C14—C15	1.495 (3)
C3—C4	1.327 (3)	C15—C16	1.326 (3)
C4—C5	1.506 (3)	C16—C17	1.501 (3)
C5—C6	1.528 (3)	C17—C18	1.512 (3)
C6—C7	1.463 (3)	C18—C19	1.471 (3)
C7—C8	1.188 (3)	C19—C20	1.189 (3)
C8—C9	1.461 (3)	C20—C21	1.463 (3)
C9—C10	1.512 (3)	C21—C22	1.513 (3)
C10—C1—C3	153.03 (19)	C22—C13—C15	153.7 (2)
C3—C1—C2	61.66 (13)	C15—C13—C14	61.79 (13)
C1—C2—C3	57.29 (13)	C13—C14—C15	57.10 (13)
C4—C3—C1	155.3 (2)	C16—C15—C13	155.5 (2)
C1—C3—C2	61.04 (13)	C13—C15—C14	61.11 (13)
C3—C4—C5	132.38 (18)	C15—C16—C17	131.77 (19)
C4—C5—C6	115.54 (17)	C16—C17—C18	116.51 (18)
C7—C6—C5	109.80 (17)	C19—C18—C17	110.20 (19)
C8—C7—C6	168.2 (2)	C20—C19—C18	168.4 (2)
C7—C8—C9	165.4 (2)	C19—C20—C21	165.2 (2)
C8—C9—C10	109.04 (17)	C20—C21—C22	108.94 (16)
C1—C10—C9	124.89 (18)	C13—C22—C21	124.75 (18)
C10—C1—C3—C4	21.6 (8)	C22—C13—C15—C16	−19.4 (8)
C1—C3—C4—C5	−8.8 (6)	C13—C15—C16—C17	4.2 (6)
C3—C4—C5—C6	−49.9 (3)	C15—C16—C17—C18	51.3 (3)
C4—C5—C6—C7	57.8 (2)	C16—C17—C18—C19	−56.9 (3)

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm. Coverage of the unique set is over 97% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections, and found to be negligible.

H atoms were placed geometrically and refined with a riding model (including free rotation about O—C bonds), and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

We thank EPSRC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1113). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*E*)- and (*Z*)-4-Ethynyl-4′-nitrostilbene

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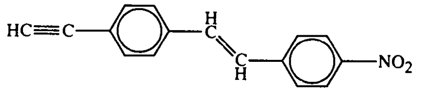
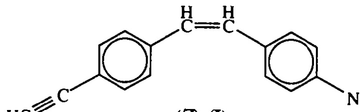
Abstract

Structural determinations of the *E* and *Z* isomers of 4-ethynyl-4′-nitrostilbene, $C_{16}H_{11}NO_2$, have been carried out, the first such studies of 'extended-chain' acetylenes bearing the prototypical NO_2 acceptor group.

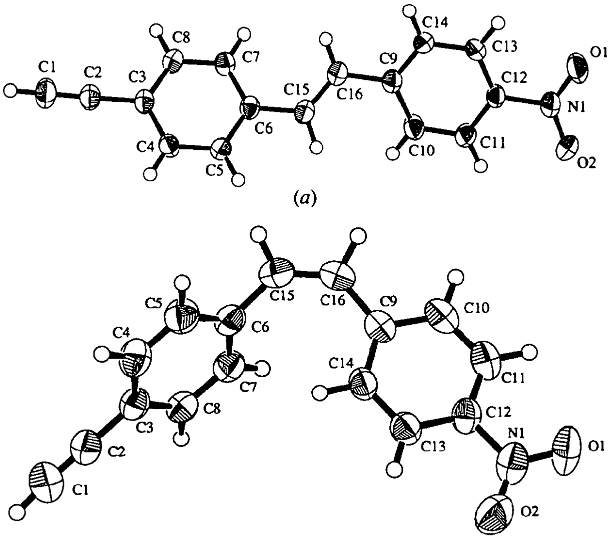
Comment

We have been investigating the non-linear optical merit of organometallic complexes (Whittall *et al.*, 1994; Whittall, Humphrey, Hockless, Skelton & White, 1995; Whittall, Humphrey, Samoc, Swiatkiewicz & Luther-Davies, 1995; Whittall, Humphrey, Persoons & Houbrechts, 1996; McDonagh, Whittall, Humphrey, Skelton & White, 1995; McDonagh *et al.*, 1996). Our utilization of the semi-empirical routine *ZINDO* (Biosym Technologies, 1994) has necessitated access to accurate molecular geometries for metal complexes and ligand fragments. We report herein the structural determinations of both the *Z* and *E* isomers of 4-ethynyl-4′-nitrostilbene, (I), which can be readily incorporated into (cyclopentadienyl)bis(phosphine)ruthenium and *trans*-chlorobis(diphosphine)ruthenium environments as the corresponding acetylide ligands (Whittall *et al.*, 1995; McDonagh *et al.*, 1995, 1996). These are the first structural studies of 'extended-chain' acetylenes bearing the prototypical NO_2 acceptor group.


(*E*)-(I)


(*Z*)-(I)

The formation of the two isomers of 4-$HC_2C_6H_4$-$CH{=}CHC_6H_4$-4′-NO_2 was carried out by coupling 4-ethynylbenzaldehyde and 4-nitrobenzyltriphenylphosphonium bromide according to standard Wittig methods. The structural studies (Fig. 1) show no significant differences in bond length and angle parameters other than those associated with the differing geometries about the alkene linkage [C(6)—C(15)—C(16) 131.5 (2) (*Z*) and 127.3 (2)° (*E*); C(15)—C(16)—C(9) 131.8 (2) (*Z*) and 124.1 (2)° (*E*)], readily explicable from phenyl–phenyl repulsion in the *Z* isomer.



(*b*)

Fig. 1. The molecular structures of (*a*) (*E*)-4-ethynyl-4′-nitrostilbene and (*b*) (*Z*)-4-ethynyl-4′-nitrostilbene, showing the labelling schemes for the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as circles of arbitrary radii.

Experimental

The title isomeric compounds were synthesized by reacting molar equivalents of 4-ethynylbenzaldehyde and 4-nitrobenzyltriphenylphosphonium bromide in methanol. A solution of sodium methoxide in methanol was added and the mixture stirred for 2 h and then cooled in ice. The resulting mixture

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