shortening C13–O3 and lengthening C13–O4. The ring formed by the dehydration of (I), C15/C20/O4/C13/C12/C11, is a chroman dihydropyran, which also has a half-chair conformation distorted towards the e,f-diplanar form. The displacement asymmetry parameter $\Delta C_2 = 0.155$ (2).

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The Mono Diels–Alder Adduct of 1,4-Bis(2,4-cyclopentadien-1-ylidene)cyclohexane and Dimethyl Butynedioate

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Abstract. Dimethyl 7-[4-(2,4-cyclopentadien-1-ylidene)cyclohexylidene]bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, $C_{22}H_{22}O_4$, $M_r = 350.4$, triclinic, $P\bar{1}$, $a = 8.215$ (1), $b = 10.6297$ (9), $c = 11.545$ (2) Å, $\alpha = 70.976$ (9), $\beta = 75.48$ (1), $\gamma = 85.245$ (8)°, $V = 922.7$ (1) Å^3, $Z = 2$, $D_x = 1.261$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1.54184$ Å, $\mu = 0.658$ mm^{-1}, $F(000) = 372$, $T = 296$ K, $R = 0.044$ for 3275 data having $F_o^2 > 3\sigma(F_o^2)$. The strained double bond *exo* to the bicyclo[2.2.1]hepta-2,5-diene has a normal bond length, 1.330 (1) Å. However, this double bond exhibits severe distortion from sp^2 hybridized geometry at the bond angle endocyclic to the bicyclo[2.2.1]hepta-2,5-diene, which is 94.76 (6)°. The cyclopentadienylidene ring is planar, with maximum deviation of 0.004 (2) Å.

Introduction. The mono Diels–Alder adduct of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane and dimethyl butynedioate, shown in Fig. 1, is one of three isomeric products expected from the stoichiometry of this reaction. Other isomers from further intramolecular Diels–Alder cycloadditions of this bifunctional dienophile to the other diene system are not observed. Dimethyl butynedioate is known to act as a bifunctional dienophile for bifunctional Diels–Alder dienes (Paquette, Wyvratt, Berk & Moerck, 1978).

The structure of the title compound is being probed to determine whether there is cooperativity of the two 'isolated' chromophores, the fulvene and the strained double bond.

Experimental. The title compound is prepared by refluxing excess 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane with dimethyl butynedioate in chloroform for 72 hours. Clear, yellow-orange crystals, m.p. 370 K, suitable for single-crystal X-ray structure determination were crystallized from hexane/ether at room temperature. The X-ray structure determination supports all standard spectroscopic measurements.

Intensity data were obtained from an irregular fragment of dimensions $0.25 \times 0.45 \times 0.50$ mm mounted in a random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at 296 K by a least-squares fit to setting angles of 25 reflections having $25 < \theta < 30°$. A hemisphere of data having $4 < 2\theta < 150°$, $0 \le h \le 10$, $-13 \le k \le 13$,
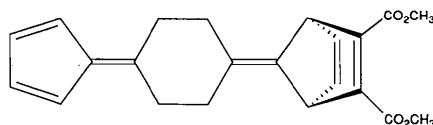

Fig. 1. The mono Diels–Alder adduct of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane and dimethyl butynedioate.

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Table 1. *Coordinates and equivalent isotropic thermal parameters*

$B_{eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha)$.

|	x	y	z	$B_{eq}(\text{Å}^2)$
O1	0·7101 (2)	0·40151 (9)	0·91901 (9)	5·41 (3)
O2	0·9611 (2)	0·4515 (1)	0·7883 (1)	8·58 (4)
O3	0·4041 (1)	0·1791 (1)	0·85314 (9)	4·68 (2)
O4	0·5055 (2)	0·1531 (1)	1·02164 (9)	5·82 (3)
C1	1·3880 (2)	−0·2967 (1)	0·7053 (1)	3·94 (3)
C2	1·5683 (2)	−0·2781 (2)	0·6541 (2)	5·45 (4)
C3	1·6322 (2)	−0·3874 (2)	0·6243 (2)	6·66 (5)
C4	1·4985 (2)	−0·4805 (2)	0·6531 (2)	5·73 (4)
C5	1·3531 (2)	−0·4290 (1)	0·7020 (1)	4·49 (3)
C6	1·2748 (2)	−0·2102 (1)	0·7440 (1)	3·97 (3)
C7	1·3194 (2)	−0·0732 (1)	0·7353 (2)	5·16 (4)
C8	1·2222 (2)	0·0316 (1)	0·6517 (2)	4·64 (3)
C9	1·0356 (2)	0·0066 (1)	0·6932 (1)	3·79 (3)
C10	0·9861 (2)	−0·1348 (1)	0·7150 (1)	4·32 (3)
C11	1·0904 (2)	−0·2380 (1)	0·7937 (1)	4·62 (3)
C12	0·9232 (2)	0·1027 (1)	0·7014 (1)	3·76 (3)
C13	0·7323 (2)	0·1072 (1)	0·7228 (1)	3·80 (3)
C14	0·7245 (2)	0·2103 (1)	0·5942 (1)	4·80 (3)
C15	0·8487 (2)	0·2950 (2)	0·5629 (1)	4·99 (4)
C16	0·9427 (2)	0·2529 (1)	0·6696 (1)	4·07 (3)
C17	0·8172 (2)	0·2716 (1)	0·7863 (1)	3·70 (3)
C18	0·6920 (2)	0·1860 (1)	0·8179 (1)	3·49 (3)
C19	0·8391 (2)	0·3823 (1)	0·8320 (1)	4·28 (3)
C20	0·7230 (3)	0·5128 (2)	0·9624 (1)	6·13 (4)
C21	0·5277 (2)	0·1720 (1)	0·9108 (1)	3·69 (3)
C22	0·2354 (2)	0·1688 (2)	0·9306 (2)	6·27 (5)
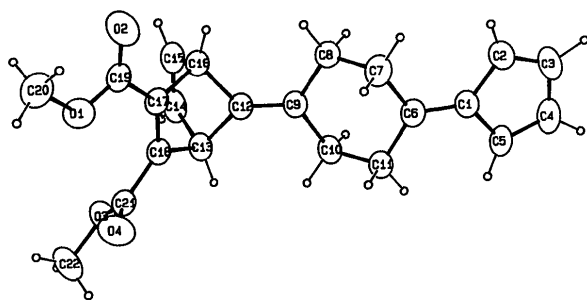
Fig. 2. *ORTEP* drawing (Johnson, 1965) of the molecule, representing C and O atoms by 40% probability ellipsoids and H atoms by circles of arbitrary radius.

$-14 \le l \le 14$ was measured using graphite-monochromated Cu $K\alpha$ radiation. The ω–2θ scans were made at speeds ranging from $0\cdot57$ to $3\cdot3°$ min^{-1} to measure all significant data with approximately equal precision. Three standard reflections (300, 020, 002) exhibited only random variation $\pm1\cdot6\%$ in intensity during data collection. Data reduction included corrections for background, Lorentz, polarization and absorption effects. The latter was based on ψ scans, with the minimum relative transmission coefficient 90·46%. Of 3806 unique data, 3275 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement.

The space group was determined by successful refinement of a centrosymmetric model. The structure was solved by direct methods and refined by full-matrix least-squares based upon F, with weights $w = 4F_o^2[\sigma^2(I) + (0\cdot02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Derermination Package* (Frenz, 1985),

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°)

O1—C19	1·318 (1)	C8—C9	1·505 (1)
O1—C20	1·447 (1)	C9—C10	1·513 (1)
O2—C19	1·194 (1)	C9—C12	1·330 (1)
O3—C21	1·333 (1)	C10—C11	1·532 (1)
O3—C22	1·439 (1)	C12—C13	1·525 (1)
O4—C21	1·1963 (9)	C12—C16	1·530 (1)
C1—C2	1·455 (1)	C13—C14	1·544 (1)
C1—C5	1·472 (1)	C13—C18	1·5446 (9)
C1—C6	1·352 (1)	C14—C15	1·318 (1)
C2—C3	1·347 (2)	C15—C16	1·540 (1)
C3—C4	1·442 (2)	C16—C17	1·537 (1)
C4—C5	1·341 (1)	C17—C18	1·331 (1)
C6—C7	1·496 (1)	C17—C19	1·477 (1)
C6—C11	1·496 (1)	C18—C21	1·482 (1)
C7—C8	1·532 (1)		
C19—O1—C20	116·25 (8)	C8—C9—C10	114·47 (7)
C21—O3—C22	116·45 (8)	C8—C9—C12	122·73 (7)
C2—C1—C5	105·20 (8)	C10—C9—C12	122·63 (7)
C2—C1—C6	127·80 (8)	C9—C10—C11	112·46 (7)
C5—C1—C6	126·98 (8)	C6—C11—C10	111·77 (7)
C1—C2—C3	108·2 (1)	C9—C12—C13	132·66 (7)
C2—C3—C4	109·42 (9)	C9—C12—C16	131·83 (8)
C3—C4—C5	108·96 (9)	C13—C12—C16	94·76 (6)
C1—C5—C4	108·22 (9)	C12—C13—C14	97·01 (7)
C1—C6—C7	123·46 (8)	C12—C13—C18	98·63 (6)
C1—C6—C11	123·77 (7)	C14—C13—C18	105·43 (6)
C7—C6—C11	112·69 (7)	C13—C14—C15	107·34 (8)
C6—C7—C8	110·46 (7)	C14—C15—C16	107·76 (8)
C7—C8—C9	112·25 (7)	C12—C16—C15	96·67 (7)
C12—C16—C17	98·58 (6)	C17—C18—C21	130·93 (6)
C15—C16—C17	105·99 (7)	O1—C19—O2	123·68 (8)
C16—C17—C18	107·46 (6)	O1—C19—C17	114·38 (7)
C16—C17—C19	120·05 (7)	O2—C19—C17	121·85 (8)
C18—C17—C19	131·97 (7)	O3—C21—O4	123·75 (8)
C13—C18—C17	107·18 (6)	O3—C21—C18	109·52 (6)
C13—C18—C21	121·32 (6)	O4—C21—C18	126·69 (8)
C2—C1—C6—C7	2·4 (2)	C10—C11—C6—C7	55·8 (2)
C6—C7—C8—C9	53·2 (2)	C11—C6—C7—C8	−57·4 (2)
C7—C8—C9—C10	−49·0 (2)	C8—C9—C12—C16	2·9 (2)
C8—C9—C10—C11	46·9 (2)	C16—C17—C19—O2	−7·2 (2)
C9—C10—C11—C6	−49·3 (2)	C13—C18—C21—O4	131·3 (2)

scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). C and O atoms were refined anisotropically; the H atoms were located by ΔF synthesis and were refined isotropically. Final $R = 0\cdot044$ ($R = 0\cdot051$ for all data), $wR = 0\cdot062$, $S = 3\cdot602$ for 324 variables. Largest shift $0\cdot08\sigma$ in the final cycle, maximum residual density $0\cdot39$ e Å^{-3}, minimum $-0\cdot34$ e Å^{-3}, extinction coefficient $g = 7\cdot0$ (6) $\times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c.

Discussion. The fractional coordinates of the title compound are given in Table 1. Fig. 2 is a perspective drawing showing the atom numbering. Distances, angles and selected torsion angles are presented in Table 2.*

The X-ray structure determination was undertaken to probe the molecule for evidence of an interaction through the carbon σ bonds that allows a significant degree of cooperativity between the two 'isolated' π-electronic systems, the strained double bond and the pentafulvene moiety. The carbon σ bonds C7—C8 and C10—C11 are 1·532 (1) Å; these bond lengths are not significantly shorter than normal sp^3–sp^3 bond lengths (March, 1985).

There is considerable distortion from ideal sp^2 hybridization at C9=C12, the double bond fusing the bicyclo[2.2.1]hepta-2,5-diene with the six-membered ring; the bond angle C13—C12—C16 is 94·76 (6)°. This degree of distortion is expected to cause this double bond to be exceptionally reactive.

The six-membered ring adopts a chair conformation. The bond angle exocyclic to the fulvene, C7—C6—C11, is 112·69 (7)° which is the same as the analogous bond angle of the precursor difulvene, 112·71 (9)° (McLaughlin, Cronan & Fronczek, 1988).

A linear C—H···O intermolecular contact exists involving carbonyl oxygen O2 and fulvene carbon C5 at x, $1-y$, z. The C···O distance is 3·351 (2) Å, the O···H distance is 2·35 (2) Å, and the angle at H is 177 (2)°. The other carbonyl oxygen, O4, has a closer intermolecular distance, 3·307 (2) Å, to the methylene

C7 at $2-x$, $-y$, $2-z$, but the H atom does not point at oxygen: O···H is 2·68 (2) Å, and the angle at H is 118 (2)°.

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Structure of *O,S*-Diacetylthiamin

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Abstract. 3-Acetylthio-4-{*N*-[4-amino-2-methyl-5-pyrimidinyl)methyl]formamido}-3-penten-1-yl acetate, $C_{16}H_{22}N_4O_4S$, $M_r = 366·45$, monoclinic, $P2_1/n$ with $a = 9·086$ (2), $b = 19·096$ (5), $c = 11·084$ (3) Å, $\beta = 98·49$ (3)°, $V = 1902·1$ (9) Å^3, $Z = 4$, $D_x = 1·279$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 16·45$ cm^{-1}, $F(000) = 776$, $T = 295$ K, $R = 0·069$ for 1341 reflections with $I \geq 2\sigma(I)$. The pyrimidine, *N*-formyl and ethylenic groups are nearly perpendicular to each other and the N(3)—C(4) bond retains single-bond character. The conformation of the molecule is stabilized by an intramolecular N(4'α)—H···O(2α) hydrogen bond [2·950 (10) Å]. The overall conformation is somewhat different from that of its congener *O,S*-dibenzoyl-

thiamin. The molecules related by a center of symmetry form a dimer *via* N(4'α)—H···N(3') hydrogen bonds [3·049 (10) Å].

Introduction. Thiamin (vitamin B$_1$) is labile against acid, alkali and heat (Dwidevi & Arnold, 1973). The thiazolium ring in thiamin is easily hydrolyzed in mildly alkaline solution to give various thiol or disulfide derivatives which, in turn, can easily be converted to thiamin upon acidification (Hopmann, 1982). Treatment of a thiol derivative of thiamin with an acylating agent such as acetic anhydride or benzoyl chloride yields the *O,S*-diacylthiamin such as *O,S*-diacetylthiamin (DAT) or *O,S*-dibenzoylthiamin (DBT). These *O,S*-diacylthiamins as well as the disulfide derivatives are potential prodrugs because they pass through

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