opposite directions when viewed along C(5)···C(7), so-called 'contra-twist', according to the values observed for the torsion angles in the six-membered ring defined by C(1), C(7), C(3), C(4), C(5) and C(6).

An interesting overall description of the title molecule can be based on the C(1)SC(2)C(3)C(4)C(5)C(6) seven-membered ring. Indeed the basic conformations of cycloheptane are the chair, twist-chair, boat and twist-boat (Hendrickson, 1961), with the twist-chair corresponding to the lowest-energy minimum (Bocian, Pickett, Rounds & Strauss, 1975).

The present seven-membered-ring conformation is similar to a distorted form of the $C_s$ chair of cycloheptane. The twisting movement is hampered by the junction between C(1), C(3) and C(5) connected *via* the C(7)H—C(8)$H_2$ group. For this ring the deformation of the chair is a result of this bridging situation with substitution at the three axial positions C(1), C(3) and C(5). The oxygen atoms O(1) and O(2) are eclipsed by C(10) and C(11) when viewed along the S—C(2) bond. Finally, in this description, whereas O(1) and C(10) occupy axial positions, the cyano group, O(2) and C(11) are equatorial.

Conformational calculations have shown that the rotational barrier around the C(1)—S bond is relatively low for compound (I) (25 kJ $mol^{-1}$). The minimum distance of 2·70 Å, between the reactive site C(2) and C(3) in (III), is at a rotation angle of 80° about this *endo* C—S bond, with regard to the X-ray determination. Cyclization induces rotation about the $\sigma$ C—S bond and a lessening of C(7)—C(1)—S and C(1)—S—C(2) angles from 117·5 and 108·5° in (I), respectively, to 104·0 and 96·6° in (III). Other structural differences between (I) and (III) are very slight, except for the lengthening of the C(3)—C(4) bond from 1·33 (1) to 1·570 (5) Å.

Intermolecular distances do not indicate any interactions except van der Waals forces.

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# Platelet Activating Factor Antagonist Design. 2. X-ray Structure of Dimethyl 2,3,4,5-Tetrahydro-5$\beta$-(3,4-methylenedioxyphenyl)-2-oxo-3$\beta$-(3,4,5-trimethoxybenzoyl)-3$\alpha$,4$\alpha$-furandicarboxylate

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**Abstract.** $C_{25}H_{24}O_{12}$, $M_r = 516{\cdot}46$, triclinic, $P\bar{1}$, $a = 8{\cdot}780$ (3), $b = 11{\cdot}298$ (4), $c = 13{\cdot}271$ (6) Å, $\alpha = 71{\cdot}77$ (4), $\beta = 70{\cdot}31$ (3), $\gamma = 72{\cdot}66$ (3)°, $V = 1189$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}44$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}74$ cm$^{-1}$, $F(000) = 540$, $T = 293$ K, final $R = 0{\cdot}046$ for 2495 observed [$F_o \geq 5\sigma(F_o)$] reflections. The observed structure reveals a *trans* disposition for the methoxycarbonyl and aryl substituents at positions 4 and 5 of the heterocycle and a *cis*-3,4-bis(methoxycarbonyl) relationship. There is no crystallographically

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imposed symmetry. Several intermolecular van der Waals interactions occur in the cell lattice of this compound.

**Introduction.** Platelet activating factor (PAF) antagonists provide a channel for elucidating the complete pathobiology of this phospholipid ether and have already yielded firm evidence for several PAF-mediated alterations of the pulmonary, intravascular and cardiovascular systems (Venuti, 1985; McManus, 1986; Etienne, Hecquet & Braquet, 1988; Smith, Rubin & Patterson, 1988). To highlight just a few of these alterations, PAF has been associated with bronchoconstriction, anaphylactic shock, increased vascular permeability, systemic hypotension, and bacterial endotoxin synergism. The binding of PAF to specific cellular receptor sites has been determined as the first step in its biological functions (McManus, 1986; Hwang, Lam, Biftu, Beattie & Shen, 1985). More potent and specific PAF receptor antagonists are now needed to probe further the important mediator role portrayed by PAF in human disease states, as well as for potential therapeutic applications. We recently began investigations aimed at the discovery of new PAF antagonists (Peterson, Smillie & Rogers, 1989) where we intend to utilize X-ray crystallography in conjunction with molecular modelling to develop an improved PAF–blood platelet receptor-site model (Cohen, 1985; Codding & Muir, 1985; Braquet & Godfroid, 1986; Godfroid & Braquet, 1986; Codding, 1988). X-ray crystallographic studies not only provide detail about the three-dimensional topography of a compound, but they also afford information on the molecular nature of the biological receptor site through an understanding of the interactions of adjacent molecules within the crystal lattice. Herein we describe the X-ray crystal structure and an analysis of the closest intermolecular contacts for dimethyl 2,3,4,5-tetrahydro-5$\beta$-(3,4-methylenedioxyphenyl)-2-oxo-3$\beta$-(3,4,5-trimethoxybenzoyl)-3$\alpha$,4$\alpha$-furandicarboxylate, a $\gamma$-lactone precursor to the enzyme inhibitory dicinnamodilactone family of lignan natural products (Kumada, Naganawa, Takeuchi, Umezawa, Yamashita & Watanabe, 1978). The dicinnamodilactones are desired as $\gamma$-lactone congeners to Merck Sharp & Dohme's potent PAF antagonists L-652,731 and L-659,989 (Wu, Biftu & Doebber, 1986; Hwang *et al.*, 1985; Biftu, Gamble, Doebber, Hwang, Shen, Snyder, Springer & Stevenson, 1986; Ponpipom, Bugianesi, Sahoo, Chabala, Hwang & Doebber, 1988), since the central atoms of the four-carbon tether between the aryl groups now would be geometrically constrained to an eclipsed orientation, and thus would provide a biological probe of this geometric effect.

**Experimental.** The title compound was obtained in 53% isolated yield by treatment of the potassium enolate of dimethyl 2,3,4,5-tetrahydro-5-(3,4-methylenedioxyphenyl)-2-oxo-3,4-furandicarboxylate (Peterson, Do & Surjasasmita, 1988) with 3,4,5-trimethoxybenzoyl chloride in tetrahydrofuran (Peterson, Do & Rogers, 1988). The product was purified by crystallization from methanol. Crystals (m.p. 432–433 K) suitable for X-ray analysis were procured by slow evaporation of a methanol solution of the pure product. The spectral and analytical data for this compound were consistent with the X-ray structure.* $D_m$ not determined. Crystal $0{\cdot}10 \times 0{\cdot}15 \times 0{\cdot}25$ mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 24 reflections ($\theta > 19{\cdot}8°$). Correction for Lorentz–polarization effect, absorption ignored. $\theta_{max} = 50°$; $h$ 0 to 10, $k$ −13 to 13, $l$ −16 to 16. Standard reflections observed every 3600 s of data collection time: 300, 060, 004. Variation $= \pm 2\%$. 4119 reflections measured, 2495 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved utilizing *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) direct-methods program. Least-squares refinement with isotropic thermal parameters led to $R = 0{\cdot}122$. The geometrically constrained H atoms were placed in calculated positions 0·95 Å from the bonded C atom and allowed to ride on that atom with $B$ fixed at 5·5 Å$^2$. The methyl H atoms were located from a difference Fourier map and included with fixed contributions ($B = 5{\cdot}5$ Å$^2$). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX*76 (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights $= [\sigma(F_o)^2 + 0{\cdot}00004F_o^2]^{-1}$, 334 parameters varied. $R = 0{\cdot}046$, $wR = 0{\cdot}046$, $S = 1{\cdot}15$. $\Delta/\sigma$ in final least-squares refinement cycle $< 0{\cdot}01$, $\Delta\rho < 0{\cdot}3$ e Å$^{-3}$ in final difference map.

**Discussion.** Fractional coordinates and $B_{eq}$ values are given in Table 1,† bond distances and angles in Table 2, and an *ORTEP* drawing (Johnson, 1976) in Fig. 1. A cell plot is provided in Fig. 2.

As required for our projected conversion of the title compound into a dicinnamodilactone, the *trans* stereochemical disposition of the 4-methoxycarbonyl and

* Physical data: IR (KBr) 3000, 2950, 2840, 1780, 1735, 1675, 1580, 1490, 1450, 1415, 1330, 1280, 1250, 1210, 1165, 1125, 1035, 1000, 910, 730 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 7·34 (*s*, 2H), 6·95–6·77 (*m*, 3H), 6·01 (*s*, 2H), 5·77 (*d*, $J = 10{\cdot}50$ Hz, 1H), 4·63 (*d*, $J = 10{\cdot}50$ Hz, 1H), 3·95 (*s*, 3H), 3·90 (*s*, 6H), 3·76 (*s*, 3H), 3·68 (*s*, 3H). Analysis: calculated for $C_{25}H_{24}O_{12}$: C 58·14, H 4·68; found: C 57·93, H 4·89.

† Lists of structure factors, anisotropic thermal parameters, least-squares-planes results, torsion angles, and final fractional coordinates for H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51588 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters for* $C_{25}H_{24}O_{12}$

| | x | y | z | $B_{eq}$*(Å²) |
|---|---|---|---|---|
| O(1) | 1·2581 (3) | 0·5501 (2) | 0·0065 (2) | 2·82 |
| O(2) | 1·1609 (3) | 0·3748 (2) | 0·0490 (2) | 3·71 |
| O(3) | 0·8372 (3) | 0·5557 (2) | 0·2429 (2) | 3·52 |
| O(4) | 1·2191 (3) | 0·3822 (2) | 0·3485 (2) | 2·86 |
| O(5) | 1·3860 (3) | 0·3347 (3) | 0·1972 (2) | 3·71 |
| O(6) | 1·3187 (3) | 0·6614 (3) | 0·2469 (2) | 3·86 |
| O(7) | 1·0540 (3) | 0·6578 (2) | 0·3357 (2) | 2·96 |
| O(8) | 1·4033 (3) | 1·0660 (2) | −0·0834 (2) | 4·19 |
| O(9) | 1·2028 (3) | 1·1439 (2) | −0·1744 (2) | 3·15 |
| O(10) | 1·0807 (3) | −0·0092 (2) | 0·3292 (2) | 2·93 |
| O(11) | 0·7950 (3) | −0·0125 (2) | 0·4825 (2) | 3·31 |
| O(12) | 0·5806 (3) | 0·2013 (2) | 0·5200 (2) | 3·26 |
| C(1) | 1·1825 (4) | 0·4578 (3) | 0·0759 (3) | 2·45 |
| C(2) | 1·1294 (4) | 0·4779 (3) | 0·1897 (2) | 1·98 |
| C(3) | 1·1430 (4) | 0·6175 (3) | 0·1666 (2) | 1·97 |
| C(4) | 1·2750 (4) | 0·6365 (3) | 0·0603 (2) | 2·32 |
| C(5) | 1·2504 (4) | 0·7713 (3) | −0·0067 (2) | 2·03 |
| C(6) | 1·3509 (4) | 0·8482 (3) | −0·0096 (3) | 2·62 |
| C(7) | 1·3214 (4) | 0·9726 (3) | −0·0672 (3) | 2·56 |
| C(8) | 1·3155 (5) | 1·1790 (3) | −0·1395 (3) | 3·50 |
| C(9) | 1·2023 (4) | 1·0184 (3) | −0·1210 (2) | 2·19 |
| C(10) | 1·1033 (4) | 0·9442 (3) | −0·1197 (3) | 2·67 |
| C(11) | 1·1291 (4) | 0·8189 (3) | −0·0601 (3) | 2·63 |
| C(12) | 0·9479 (4) | 0·4619 (3) | 0·2463 (3) | 2·43 |
| C(13) | 0·9133 (4) | 0·3342 (3) | 0·3051 (2) | 2·20 |
| C(14) | 1·0237 (4) | 0·2220 (3) | 0·2863 (3) | 2·34 |
| C(15) | 0·9826 (4) | 0·1059 (3) | 0·3441 (3) | 2·33 |
| C(16) | 0·8332 (4) | 0·1021 (3) | 0·4217 (3) | 2·49 |
| C(17) | 0·7232 (4) | 0·2150 (3) | 0·4413 (3) | 2·46 |
| C(18) | 0·7613 (4) | 0·3314 (3) | 0·3827 (3) | 2·39 |
| C(19) | 1·2479 (4) | 0·3919 (3) | 0·2555 (3) | 2·13 |
| C(20) | 1·5077 (6) | 0·2563 (6) | 0·2553 (4) | 6·81 |
| C(21) | 1·1840 (5) | 0·6486 (3) | 0·2531 (3) | 2·43 |
| C(22) | 1·0845 (5) | 0·6670 (4) | 0·4302 (3) | 4·05 |
| C(23) | 1·2453 (5) | −0·0113 (4) | 0·2624 (3) | 3·67 |
| C(24) | 0·7319 (5) | −0·0728 (4) | 0·4331 (3) | 4·11 |
| C(25) | 0·4678 (5) | 0·3144 (4) | 0·5467 (3) | 3·80 |

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

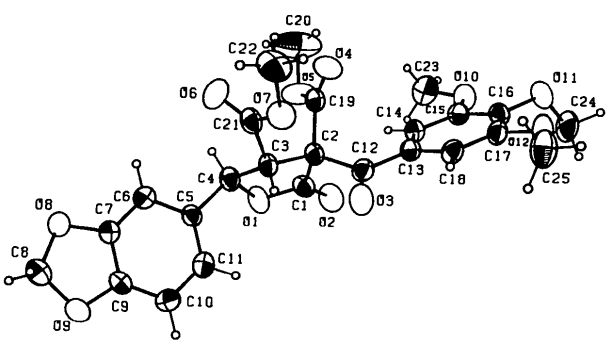


Fig. 1. Thermal-ellipsoid plot of the title compound showing the atom-numbering scheme. H-atom radii are arbitrarily reduced.

Table 2. *Bond distances* (Å) *and angles* (°) *for* $C_{25}H_{24}O_{12}$

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1·341 (4) | O(1)–C(4) | 1·460 (4) |
| O(2)–C(1) | 1·192 (4) | O(3)–C(12) | 1·206 (4) |
| O(4)–C(19) | 1·190 (4) | O(5)–C(19) | 1·315 (4) |
| O(5)–C(20) | 1·460 (5) | O(6)–C(21) | 1·205 (4) |
| O(7)–C(21) | 1·315 (4) | O(7)–C(22) | 1·450 (4) |
| O(8)–C(7) | 1·371 (4) | O(8)–C(8) | 1·418 (4) |
| O(9)–C(8) | 1·428 (4) | O(9)–C(9) | 1·377 (4) |
| O(10)–C(15) | 1·363 (4) | O(10)–C(23) | 1·424 (4) |
| O(11)–C(16) | 1·370 (4) | O(11)–C(24) | 1·413 (4) |
| O(12)–C(17) | 1·363 (4) | O(12)–C(25) | 1·429 (4) |
| C(1)–C(2) | 1·542 (4) | C(2)–C(3) | 1·541 (4) |
| C(2)–C(12) | 1·558 (4) | C(2)–C(19) | 1·524 (4) |
| C(3)–C(4) | 1·526 (4) | C(3)–C(21) | 1·513 (4) |
| C(4)–C(5) | 1·508 (4) | C(5)–C(6) | 1·397 (4) |
| C(5)–C(11) | 1·377 (4) | C(6)–C(7) | 1·376 (4) |
| C(7)–C(9) | 1·364 (4) | C(9)–C(10) | 1·371 (4) |
| C(10)–C(11) | 1·390 (5) | C(12)–C(13) | 1·480 (4) |
| C(13)–C(14) | 1·384 (4) | C(13)–C(18) | 1·401 (4) |
| C(14)–C(15) | 1·385 (4) | C(15)–C(16) | 1·386 (4) |
| C(16)–C(17) | 1·392 (5) | C(17)–C(18) | 1·381 (4) |

| | | | |
|---|---|---|---|
| C(1)–O(1)–C(4) | 111·6 (2) | C(19)–O(5)–C(20) | 114·7 (3) |
| C(21)–O(7)–C(22) | 115·7 (3) | C(7)–O(8)–C(8) | 105·6 (3) |
| C(8)–O(9)–C(9) | 105·0 (3) | C(15)–O(10)–C(23) | 117·8 (3) |
| C(16)–O(11)–C(24) | 114·5 (3) | C(17)–O(12)–C(25) | 117·7 (3) |
| O(1)–C(1)–O(2) | 122·6 (3) | O(1)–C(1)–C(2) | 110·3 (3) |
| O(2)–C(1)–C(2) | 127·1 (3) | C(1)–C(2)–C(3) | 101·1 (2) |
| C(1)–C(2)–C(12) | 110·4 (3) | C(3)–C(2)–C(12) | 111·4 (3) |
| C(1)–C(2)–C(19) | 112·6 (3) | C(3)–C(2)–C(19) | 109·2 (3) |
| C(12)–C(2)–C(19) | 111·7 (3) | C(2)–C(3)–C(4) | 104·0 (2) |
| C(2)–C(3)–C(21) | 114·4 (3) | C(4)–C(3)–C(21) | 112·6 (3) |
| O(1)–C(4)–C(3) | 103·7 (2) | O(1)–C(4)–C(5) | 109·9 (3) |
| C(3)–C(4)–C(5) | 113·5 (3) | C(4)–C(5)–C(6) | 117·6 (3) |
| C(4)–C(5)–C(11) | 121·5 (3) | C(6)–C(5)–C(11) | 120·9 (3) |
| C(5)–C(6)–C(7) | 116·7 (3) | O(8)–C(7)–C(6) | 128·0 (3) |
| O(8)–C(7)–C(9) | 109·9 (3) | C(6)–C(7)–C(9) | 122·0 (3) |
| O(8)–C(8)–O(9) | 108·0 (3) | O(9)–C(9)–C(7) | 110·0 (3) |
| O(9)–C(9)–C(10) | 127·9 (3) | C(7)–C(9)–C(10) | 122·1 (3) |
| C(9)–C(10)–C(11) | 116·7 (3) | C(5)–C(11)–C(10) | 121·6 (3) |
| O(3)–C(12)–C(2) | 118·6 (3) | O(3)–C(12)–C(13) | 121·1 (3) |
| C(2)–C(12)–C(13) | 120·3 (3) | C(12)–C(13)–C(14) | 122·8 (3) |
| C(12)–C(13)–C(18) | 116·5 (3) | C(14)–C(13)–C(18) | 120·7 (3) |
| C(13)–C(14)–C(15) | 119·6 (3) | O(10)–C(15)–C(14) | 123·9 (3) |
| O(10)–C(15)–C(16) | 115·9 (3) | C(14)–C(15)–C(16) | 120·2 (3) |
| O(11)–C(16)–C(15) | 120·5 (3) | O(11)–C(16)–C(17) | 119·4 (3) |
| C(15)–C(16)–C(17) | 120·1 (3) | O(12)–C(17)–C(16) | 115·7 (3) |
| O(12)–C(17)–C(18) | 124·1 (3) | C(16)–C(17)–C(18) | 120·2 (3) |
| C(13)–C(18)–C(17) | 119·2 (3) | O(4)–C(19)–O(5) | 124·6 (3) |
| O(4)–C(19)–C(2) | 122·9 (3) | O(5)–C(19)–C(2) | 112·4 (3) |
| O(6)–C(21)–O(7) | 125·1 (3) | O(6)–C(21)–C(3) | 124·1 (3) |
| O(7)–C(21)–C(3) | 110·7 (3) | | |

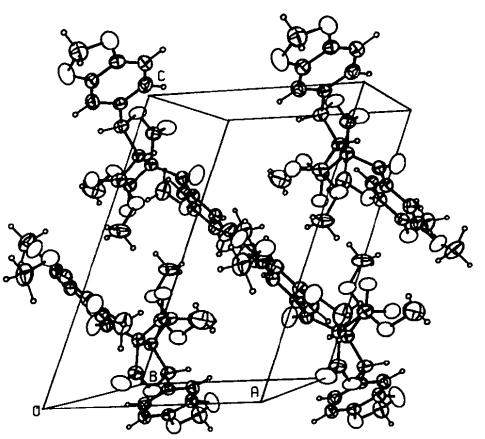


Fig. 2. Cell plot of the title compound.

5-aryl moieties was preserved during the α-aroylation reaction (Peterson, Do & Rogers, 1988). The C(5)–C(4)–C(3)–C(21) torsion angle of −86·4° and the large vicinal hydrogen coupling constant of 10·50 Hz between C(4)–H and C(3)–H are in accord with this assignment. The *ORTEP* diagram also reveals that approach of the aroyl chloride [which ultimately becomes the C(2) aroyl group] to the enolate anion occurs preferentially from the sterically least congested face of the γ-lactone ring, affording a *cis*-bis(methoxycarbonyl) array. Consistent with this finding are C(21)–C(3)–C(2)–C(19) and C(21)–C(3)–C(2)–C(12) torsion angles of −31·7 and 92·1°, respectively.

Similarly, the C(4)–C(3)–C(2)–C(1) torsion angle is −27·4°. The pseudo-*gauche* relationship that exists about atoms C(2) and C(3) in the title compound differs from the orientation for the analogous ring C atoms in L-652,731 and L-659,989 (Wu *et al.*, 1986; Hwang *et al.*, 1985; Biftu *et al.*, 1986; Ponpipom *et al.*, 1988), in that atoms C(12) and C(4) are now nearly *anti* to one another, Fig. 3.

The lactone ring atoms C(1), O(1), C(2) and C(4) define a plane to within 0·017 Å while C(3) deviates from this plane by 0·473 Å. A separate plane intersects the lactone ring plane at an angle of 1·72° and encompasses atoms C(1), O(1), O(2) and C(2). These atoms are planar to within 0·004 Å and C(4) and C(3) deviate from this plane by −0·066 and 0·422 Å, respectively. The 5-aryl ring atoms C(5) through C(11) and O(8) and O(9) are planar to within 0·099 Å, and this plane intersects the C(1), O(1), C(2), C(4) plane at an angle of 115·79°. The 3-aryl C atoms C(13) through C(18) also describe a plane to within 0·008 Å. The latter plane intersects that described by C(2), C(12), C(13) and O(3), which itself is within 0·008 Å of planarity, at an angle of 21·23°. There is some bond-angle compression about C(2), C(3) and C(4) from that usually associated with $sp^3$-hybridized carbon because of the ring geometry in this compound. The angle C(1)–C(2)–C(3) is 101·1 (2)°, C(2)–C(3)–C(4) is 104·0 (2)°, and O(1)–C(4)–C(3) is 103·7 (2)°. The C(2)–C(3)–C(21), C(3)–C(2)–C(12) and C(3)–C(4)–C(5) bond angles broaden to 114·4 (3), 111·4 (3) and 113·5 (3)°, respectively, as a result of this geometric angle compression. Bond lengths between ring atoms C(2) through C(4) are normal, however. The distance C(2)–C(3) is 1·541 (4) Å and C(3)–C(4) is 1·526 (4) Å.

An analysis of the closest intermolecular contact distances reveals that van der Waals forces are likely to be the dominant stabilizing force in the crystal lattice. Several interactions were noted to occur between neighboring molecules. The non-hydrogen to hydrogen contact distances from O(3) to H(1)C(8) and H(2)C(8) on a molecule related to that in Table 1 by 2−*x*, 2−*y*, −*z* are 2·72 and 2·76 Å, respectively, while the O(9) to H(1)C(3) separation is 2·48 Å. The corresponding O(9) to O(3) intermolecular distance is 3·168 (4) Å. The distance from O(8) to H(1)C(6) on another molecule at 3−*x*, 2−*y*, −*z* is 2·63 Å, whereas the O(8) to O(8) separation is 3·053 (6) Å. At closest contact, O(4) lies 2·38 Å from H(2)C(22) on a molecule at 2−*x*, 1−*y*, 1−*z*, while H(1)C(18) and H(3)C(22) are separated by 2·80 Å. For a molecule at 2−*x*, 1−*y*, −*z*, the distance O(2) to H(1)C(11) is 2·81 Å, O(9) to H(3)C(24) is 2·71 Å, and O(10) to H(1)C(10) is 2·68 Å. Other noticeably shorter non-hydrogen to hydrogen contact distances include O(12) to H(1)C(24) at 2·63 Å for a molecule at 1−*x*, −*y*, 1−*z*, and the O(2) to H(1)C(8) and O(10) to H(1)C(22) separations of 2·66 and 2·64 Å, respectively, on a neighboring molecule at *x*, *y*−1, *z*.

van der Waals interactions of these types may prove to be important for the binding of an antagonist to the PAF–platelet receptor site. Investigations of several other analogues of L-652,731 and L-659,989 are now in progress in our laboratory to ascertain the utility of this approach to the design of more potent and specific antagonists and an improved drug–receptor-site model.

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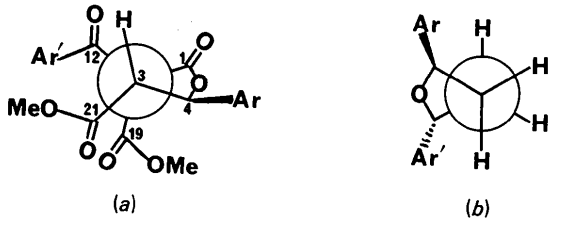


Fig. 3. Pseudo-*gauche* orientations of (*a*) the title compound (Ar = 3,4-methylenedioxyphenyl; Ar′ = 3,4,5-trimethoxyphenyl) and (*b*) L-652,731 (Ar = Ar′ = 3,4,5-trimethoxyphenyl).

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# 5-(2,4-Cyclopentadien-1-ylidene)cyclooctanone, a Bichromophoric Molecule

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**Abstract.** $C_{13}H_{16}O$, $M_r = 188{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}7499\ (12)$, $b = 12{\cdot}552\ (2)$, $c = 15{\cdot}021\ (3)$ Å, $V = 1084{\cdot}1\ (6)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}153$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}066$ mm$^{-1}$, $F(000) = 408$, $T = 295$ K, $R = 0{\cdot}032$ for 1040 data having $F_o^2 > 1\sigma(F_o^2)$. The title molecule adopts a boat-chair conformation also found for 1,5-cyclooctadione [Miller & McPhail (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 1527–1531]. There are considerable bond-angle distortions observed for all the methylenes forming the eight-membered ring. These six bond angles range from 111·9 (2)–115·8 (2)°. The bond angle exocyclic to the cyclopentadienylidene ring is 116·6 (2)°. The non-bonding distance between the O and the electrophilic fulvene C is 3·636 (2) Å. The cyclopentadienylidene ring is planar, with maximum deviation of 0·002 (2) Å.

**Introduction.** The title molecule (Fig. 1) is being studied as part of an investigation of bichromophoric molecules. The two $\pi$-electronic systems of the title molecule are 'isolated' from each other by two trimethylene chains. Bichromophoric effects among flexible molecules are frequently most intense when the two chromophores are separated by this chain length (De Schryver, Boens & Put, 1977). This X-ray structure determination was undertaken to determine if any significant ground state–ground state interactions are detectable in this molecule.

**Experimental.** The title compound was prepared by condensation of 1,5-cyclooctadione with one equivalent of freshly distilled 1,3-cyclopentadiene, catalyzed with pyrrolidine in methanol at room temperature (Stone & Little, 1985). Clear, yellow crystals, m.p. 358 K, were grown by sublimation at room temperature and 0·01 mm Hg. All standard spectroscopic measurements can be interpreted from the X-ray structure.

Intensity data were obtained from an irregular fragment of dimensions 0·18 × 0·35 × 0·40 mm mounted in a random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at 295 K by a least-squares fit to setting angles of 25 reflections having $10 < \theta < 12°$. Two octants of data having $2 < 2\theta < 55°$, $0 \le h \le 7$, $0 \le k \le 16$, $-19 \le l \le 19$, were measured using graphite-monochromated Mo $K\alpha$ radiation. $\omega$–$2\theta$ scans were made at speeds ranging from 0·45 to 4·0° min$^{-1}$ to measure all significant data with approximately equal precision. Three standard reflections (200, 020, 004) declined in intensity by 2·7% during data collection, and a linear correction was applied. Data reduction also included corrections for background, Lorentz and polarization effects. Absorption was negligible. The two equivalent octants of data were averaged ($R_{int} = 0{\cdot}023$) to yield 1465 unique data of which 1040 had $F_o^2 > 1\sigma(F_o^2)$ and were used in the refinement.

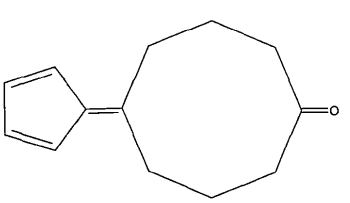


Fig. 1. 5-(2,4-Cyclopentadien-1-ylidene)cyclooctane.

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