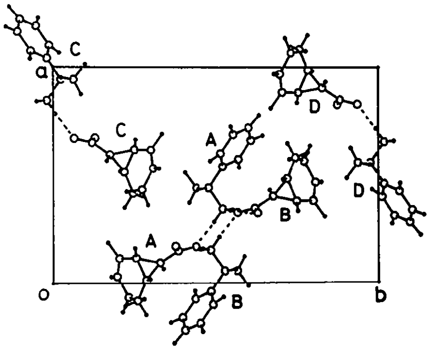

Fig. 2. The crystal structure of (I) viewed along the *c* axis. The hydrogen bonds are indicated by broken lines. Symmetry code: (*A*) x, y, z; (*B*) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (*C*) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (*D*) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

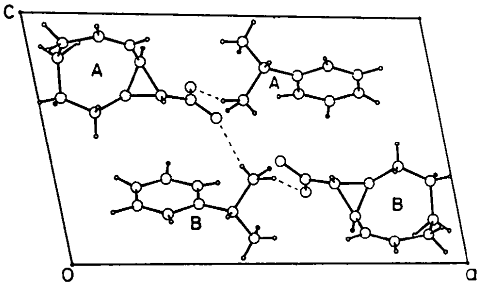

Fig. 3. The crystal structure of (II) viewed along the *b* axis. The hydrogen bonds are indicated by broken lines. Symmetry code: (*A*) x, y, z; (*B*) $1-x, -\frac{1}{2}+y, 1-z$.

Table 3. *Hydrogen-bond distances* (Å)

Compound (I)		Compound (II)	
N(1)–H···O(1)	2·767 (3)	N(1)–H···O(1)	2·679 (5)
N(1)–H···O(2^{i})	2·717 (3)	N(1)–H···O(2^{iii})	2·733 (5)
N(1)–H···O(2^{iii})	2·766 (3)	N(1)–H···O(2^{iv})	2·793 (4)

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

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Substituent Effects of π Acceptors to Prismane. Structure of Methyl 2,3,5,6-Tetramethyl-4-phenylprismanecarboxylate* and Theoretical Calculations on Formylprismane

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Abstract. $C_{18}H_{20}O_2$, $M_r = 268·36$, triclinic, $P\bar{1}$, $a = 7·275$ (1), $b = 10·244$ (2), $c = 10·350$ (2) Å, $\alpha = 81·20$ (2), $\beta = 80·63$ (2), $\gamma = 77·70$ (2)°, $V = 738·0$ (3) Å^3, $Z = 2$, $D_x = 1·21$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 0·0720$ mm^{-1}, $F(000) = 288$, $T = 89$ (2) K, $R = 0·059$ for 2632 unique observed reflections $[I > 3\sigma(I)]$. The carbonyl group in the title compound has a nearly bisected conformation relative to the adjacent three-membered ring of the prismane system. This is attributed to favourable electronic interactions. As a result the distal bond of this ring is shortened [1·499 (2) Å] and the vicinal bonds are lengthened [1·541 (2) and 1·564 (2) Å]. MO and *ab*

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* IUPAC name: methyl 2,3,5,6-tetramethyl-4-phenyltetracyclo-[2.2.0.0^{2,6}.0^{3,5}]hexanecarboxylate.

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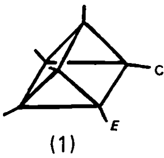
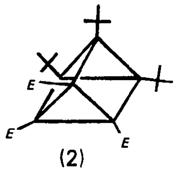
initio calculations on the model compound formylprismane reproduced the bond-length alternation found by X-ray investigations reasonably well.

Introduction. The structure of methyl 2,3,5,6-tetramethyl-4-phenylprismanecarboxylate (1) has been established as part of an investigation into the bonding in polycyclic small-membered rings and the electronic influence of substituents on the molecular dimensions of these compounds (Maier, Bauer, Huber-Patz, Jahn, Kallfass, Rodewald & Irngartinger, 1986).



(1)



(2)

$E = CO_2CH_3$

Experimental. Compound (1) was synthesized according to Dopper, Greijdanus & Wynberg (1975). Colourless prisms 0·4 × 0·5 × 0·3 mm, crystallized from *n*-pentane/ether solution. Data measured on an Enraf–Nonius CAD-4 diffractometer. ω–2θ-scan method, cell dimensions from 2θ angles of 25 high order reflections ($20 < 2\theta < 34°$), 3340 data up to $\sin\theta/\lambda = 0·70$ Å^{-1}, $0 < h < 9$, $-11 < k < 13$, $-12 < l < 13$, 3170 unique reflections, 3 standard reflections: 335, 342, 234 (loss in intensity: 15% in 2 days), 2632 intensities with $I > 3\sigma(I)$, $R_{\rm int} = 0·042$. Absorption ignored.

The structure was solved using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) with a previous room-temperature dataset. The structure was refined with the data measured at 89 K by full-matrix least squares on F^2 with anisotropic thermal parameters for C and O atoms; H atoms located from difference Fourier syntheses and refined isotropically. 261 parameters, $R = 0·059$ for 2632 observed reflections, $wR = 0·076$, $w = 4F^2/\sigma^2(F^2) + (0·03F^2)^2$, $S = 3·749$, $(\Delta/\sigma)_{\rm max} < 0·01$, largest peak $= 0·58$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SDP* programs (Frenz, 1982) used on a PDP 11/44.

Discussion. The final atomic parameters for (1) are given in Table 1.* Bond lengths and bond angles are listed in Table 2. The atom-numbering system is shown in Fig. 1.

In the three-membered ring C(1),C(2),C(6), substituted by the methoxycarbonyl group, one bond [C(1)–C(6) 1·499 (2) Å] is short and two bonds [C(1)–C(2) 1·541 (2), C(2)–C(6) 1·564 (2) Å] are long. These differences are probably caused by the π-acceptor properties of the ester group. Such effects

Table 1. *Atomic coordinates and thermal parameters* (Å^2 × 10^4)

$U_{\rm eq}$ is one-third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	$U_{\rm eq}$
O(1)	0·78867 (19)	0·38584 (12)	0·38733 (12)	303 (8)
O(2)	0·82697 (16)	0·16123 (11)	0·43689 (11)	213 (7)
C(1)	0·63327 (22)	0·35073 (16)	0·13259 (15)	180 (9)
C(2)	0·65591 (22)	0·26173 (15)	0·26542 (15)	179 (9)
C(3)	0·60176 (21)	0·14342 (15)	0·21224 (15)	167 (9)
C(4)	0·58254 (21)	0·22994 (15)	0·07938 (15)	169 (9)
C(5)	0·41026 (22)	0·23304 (16)	0·18502 (16)	195 (9)
C(6)	0·46285 (23)	0·35422 (16)	0·23610 (16)	198 (9)
C(7)	0·74087 (24)	0·45733 (16)	0·06828 (17)	221 (10)
C(8)	0·34668 (28)	0·46380 (18)	0·31059 (18)	283 (11)
C(9)	0·60883 (23)	0·18986 (17)	−0·05580 (16)	213 (9)
C(10)	0·22423 (24)	0·19487 (19)	0·18212 (18)	273 (11)
C(11)	0·65543 (21)	−0·00372 (15)	0·24218 (15)	167 (9)
C(12)	0·81326 (23)	−0·07611 (17)	0·17036 (17)	212 (9)
C(13)	0·86486 (24)	−0·21405 (17)	0·19858 (17)	237 (10)
C(14)	0·76073 (24)	−0·28401 (16)	0·29958 (17)	228 (10)
C(15)	0·60314 (24)	−0·21310 (17)	0·37158 (17)	236 (10)
C(16)	0·55045 (23)	−0·07545 (16)	0·34288 (16)	202 (9)
C(17)	0·76294 (23)	0·27835 (16)	0·36616 (16)	190 (9)
C(18)	0·92409 (27)	0·17280 (20)	0·54473 (18)	303 (11)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1)–C(17)	1·213 (2)	C(3)–C(11)	1·472 (2)
O(2)–C(17)	1·340 (2)	C(4)–C(5)	1·521 (2)
O(2)–C(18)	1·446 (2)	C(4)–C(9)	1·489 (2)
C(1)–C(2)	1·541 (2)	C(5)–C(6)	1·561 (3)
C(1)–C(4)	1·562 (3)	C(5)–C(10)	1·493 (3)
C(1)–C(6)	1·499 (2)	C(6)–C(8)	1·489 (2)
C(1)–C(7)	1·490 (2)	C(11)–C(12)	1·396 (2)
C(2)–C(17)	1·448 (3)	C(11)–C(16)	1·398 (2)
C(2)–C(3)	1·551 (3)	C(12)–C(13)	1·381 (2)
C(2)–C(6)	1·564 (2)	C(13)–C(14)	1·387 (2)
C(3)–C(4)	1·527 (2)	C(14)–C(15)	1·389 (2)
C(3)–C(5)	1·538 (2)	C(15)–C(16)	1·379 (2)
C(17)–O(2)–C(18)	114·8 (1)	C(5)–C(4)–C(9)	129·1 (2)
C(2)–C(1)–C(4)	88·6 (1)	C(4)–C(5)–C(3)	59·9 (1)
C(2)–C(1)–C(6)	61·9 (1)	C(3)–C(5)–C(6)	91·1 (1)
C(2)–C(1)–C(7)	128·1 (2)	C(3)–C(5)–C(10)	129·7 (1)
C(4)–C(1)–C(6)	90·3 (1)	C(4)–C(5)–C(6)	89·5 (1)
C(4)–C(1)–C(7)	132·1 (1)	C(4)–C(5)–C(10)	129·5 (2)
C(6)–C(1)–C(7)	131·5 (1)	C(6)–C(5)–C(10)	132·2 (1)
C(1)–C(2)–C(3)	90·9 (1)	C(1)–C(6)–C(2)	60·4 (1)
C(6)–C(2)–C(1)	57·7 (1)	C(1)–C(6)–C(5)	90·5 (1)
C(1)–C(2)–C(17)	127·3 (1)	C(1)–C(6)–C(8)	132·1 (2)
C(3)–C(2)–C(6)	90·5 (1)	C(2)–C(6)–C(5)	88·5 (1)
C(3)–C(2)–C(17)	137·1 (1)	C(2)–C(6)–C(8)	128·0 (2)
C(6)–C(2)–C(17)	124·3 (1)	C(5)–C(6)–C(8)	132·1 (2)
C(2)–C(3)–C(4)	89·5 (1)	C(3)–C(11)–C(12)	120·8 (1)
C(2)–C(3)–C(5)	89·8 (1)	C(3)–C(11)–C(16)	121·3 (1)
C(2)–C(3)–C(11)	132·5 (1)	C(12)–C(11)–C(16)	117·9 (1)
C(5)–C(3)–C(4)	59·5 (1)	C(11)–C(12)–C(13)	121·0 (1)
C(4)–C(3)–C(11)	129·6 (1)	C(12)–C(13)–C(14)	120·6 (1)
C(5)–C(3)–C(11)	130·5 (1)	C(13)–C(14)–C(15)	118·9 (1)
C(1)–C(4)–C(3)	91·0 (1)	C(14)–C(15)–C(16)	120·6 (2)
C(1)–C(4)–C(5)	89·7 (1)	C(11)–C(16)–C(15)	121·0 (1)
C(1)–C(4)–C(9)	132·0 (1)	O(1)–C(17)–O(2)	123·2 (2)
C(3)–C(4)–C(5)	60·6 (1)	O(1)–C(17)–C(2)	124·4 (1)
C(3)–C(4)–C(9)	130·2 (1)	O(2)–C(17)–C(2)	112·4 (1)

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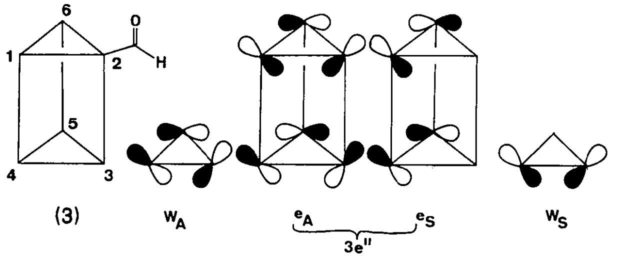
* Lists of H-atom positions and the corresponding bond distances and angles, anisotropic thermal parameters of non-H atoms, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43368 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

have been observed in cyclopropane derivatives (Allen, 1980). The carbonyl group C(17)=O(1) has an approximately bisected conformation (π orbitals of the carbonyl group parallel to the Walsh orbitals of the three-membered ring). The torsion angle $\tau[X(1)\cdots C(2)$–$C(17)$–$O(1)]$ is −7·6°, where $X(1)$ is the centre of the distal bond C(1)–C(6). This conformation allows a favourable interaction between the π system of the carbonyl group and the $3e''$ orbital of the prismane (Newton, Schulman & Manus, 1974). The shortening (d_n) of the distal bond by 0·036 Å, relative to average bond lengths ($\Delta = 1{\cdot}535$ Å), of this three-membered ring is larger than the corresponding value in cyclopropanes [$d_n = 0{\cdot}026\,(5)$ Å, $\Delta = 1{\cdot}504\,(3)$ Å]. The bond C(2)–C(17) [1·448 (3) Å] is also shortened, compared with the corresponding bond in cyclopropane derivatives [1·481 (3) Å] and indicates a comparatively strong interaction between the prismane and the carbonyl group. These electronic interactions were not found in the prismane derivative (2) because of the unfavourable orientation of the ester groups [$\tau = 136{\cdot}0\,(3)$°, C(three-membered ring)–CO 1·484 (3), C–C(ring) 1·521 (3) Å; Maier *et al.* (1986)]. Similar effects are not observed in the three-membered ring substituted by the phenyl ring [C(3),C(4),C(5)], because it has a nearly perpendicular conformation (π orbitals of the phenyl ring perpendicular to the Walsh orbitals of the three-membered ring) [$X(2)\cdots C(3)$–$C(11)$–$C(12)$ 87·7 (2)°, $X(2)\cdots C(3)$–$C(11)$–$C(16)$ −92·2 (2)°, where $X(2)$ is the centre of the distal bond]. The bond lengths in the four-membered rings [1·551 (3) to 1·562 (3) Å] connecting the three-membered rings have the same magnitude as in the prismane derivative (2) [1·560 (3) Å] and in hexamethylprismane [1·551 (5) Å by electron diffraction; Karl, Wang & Bauer (1975)].



(3)

To rationalize the results of our X-ray investigations we have carried out molecular orbital (MO) calculations using formylprismane (3) as a model for (1). Applying the MNDO procedure (Dewar & Thiel, 1977) and minimizing all geometrical parameters with respect to the heat of formation, we obtained for (3) the bisected conformation of the formyl group (C_s point group) as indicated above. It is found that in the 'upper' three-membered ring of (3) [C(1),C(2),C(6)] the substitution by the formyl group shortens one bond [C(1)–C(6) 1·55 Å] and lengthens two bonds [C(1)–C(2) and C(2)–C(6) 1·56 Å]. The bond lengths of the lower three-membered ring [C(3)–C(4), C(3)–C(5), C(4)–C(5) 1·55 Å] are predicted to be equal. About the same bond lengths result for C(1)–C(4), C(5)–C(6) 1·55 and C(2)–C(3) 1·56 Å. The same pattern, *i.e.* bond alternation in the upper part and no bond alternation in the lower part of the prismane skeleton is found when we apply a minimal-basis-set (STO-3G; Binkley, Whiteside, Hariharan, Seeger, Pople, Hehre & Newton, 1978) *ab initio* procedure. Both theoretical procedures reproduce the bond-length alternation found by the X-ray investigations reasonably well. The magnitudes of the bond lengths calculated are not directly comparable with the X-ray results.

To find out the reasons for these alternations we consider the wave function of the highest molecular orbital (HOMO) of prismane ($3e''$). Sketches of the symmetry-adapted wave functions are given above. Both can be described as the antisymmetric linear combinations of the Walsh type (W_A, W_S) orbitals of a cyclopropane unit. Attaching a CO group, say at C(2) of the prismane skeleton, leads to an interaction between the HOMO of the prismane with the LUMO (π^*) of the CO group. For symmetry reasons only one linear combination (e_A) of the HOMO interacts, while the other one (e_S) remains essentially unaffected. This interaction leads to a stabilization of e_A and a destabilization of π^* of the CO group. In the resulting wave function ($e_A + \pi^*$) the coefficients of the atomic orbitals at the 'lower' part of the prismane skeleton are decreased compared with those at the 'upper' part (arguments based on the second-order pertubation theory) (Heilbronner & Bock, 1968; Dewar & Dougherty, 1975).

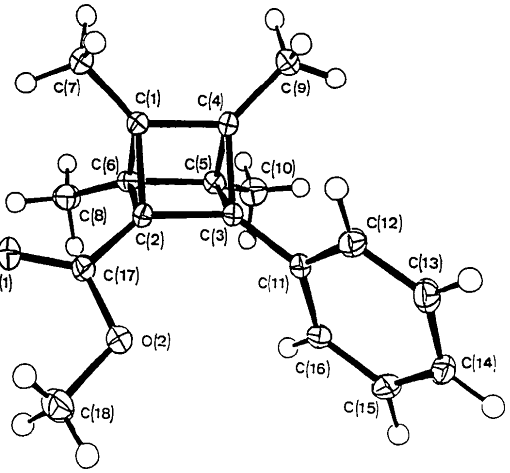


Fig. 1. *ORTEP* (Johnson, 1976) plot of compound (1) with 50% probability thermal ellipsoids.

The interaction between e_A of the prismane part and π^* of the CO group causes an electron transfer from the prismane, especially the upper three-membered ring moiety, to the CO group. As a consequence the antibonding character of C(1)—C(6) and the bonding character of C(1)—C(2) and C(2)—C(6), respectively, are reduced. This leads to the bond alternation for (3).

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Structure and Stereochemistry of 2-(*N*-Methylaniline)-3-(*N*-methoxyaceto)-7-(*p*-chlorophenyl)-8-methoxy-4,5-benzo-3-aza-1-nonem*†

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Abstract. $C_{28}H_{26}ClN_3O_4$, $M_r = 504{\cdot}0$, monoclinic, $P2_1/n$, $a = 7{\cdot}468$ (3), $b = 33{\cdot}316$ (8), $c = 10{\cdot}467$ (4) Å, $\beta = 100{\cdot}28$ (3)°, $Z = 4$, $D_x = 1{\cdot}31$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}184$ mm^{-1}, $F(000) = 1056$, $T = 293$ K, final $R = 0{\cdot}075$ for 2003 reflections. The structure established chemically is confirmed. The seven-membered ring adopts a boat-shaped conformation. The dihedral angles between the best planes through the methoxyacetyl group and the phenyl ring of the *N*-methylanilino group at C(2), and between the *p*-chlorophenyl ring and methoxy group at C(8) are 128·0 (8) and 53·6 (8)°, respectively, and thus reduce the crowding of these bulky groups on the diazepine ring. The packing in the crystal is entirely due to van der Waals forces.

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* 2a-(*p*-Chlorophenyl)-2-methoxy-5-(2-methoxyacetyl)-4-(*N*-methylanilino)-1,2,2a,5-tetrahydroazeto[1,2-*a*][1,5]benzodiazepin-1-one.

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