

Il est remarquable de constater que les liaisons C—H obtenues avec les atomes d'hydrogène affinés sans contraintes restent proches de 0,95 Å et les angles obtenus pour les liaisons sp^3 et sp^2 de 109 et 120°.*

Les angles de torsion H(2)C(2)C(3)H(3), H(3)-C(3)C(4)H(41) et H(3)C(3)C(4)H(42) sont -112 (2), 58 (2) et 169 (2)°; une analyse rapide des spectres de RMN avait conduit à des valeurs approchées de ± 100 , ± 30 et $\pm 150^\circ$ (Zervos & Wartski, 1986).

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* La valeur des liaisons et angles entre atomes (y compris les atomes d'hydrogène), les listes des facteurs de structure et des facteurs d'agitations thermiques anisotropes ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 43232: 24 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Structures of (Z)- and (E)-1,2-Diphenyl-2-(4-tolylvinyl) Bromide

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Abstract. $C_{21}H_{17}Br$, $M_r = 394.27$. (*E*)-isomer: triclinic, $P\bar{1}$, $a = 17.454$ (4), $b = 9.763$ (3), $c = 10.574$ (2) Å, $\alpha = 75.85$ (2), $\beta = 79.62$ (2), $\gamma = 77.56$ (2)°, $V = 1690.58$ Å³, $Z = 4$, $D_x = 1.37$, $D_m = 1.34$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.00$ cm⁻¹, $F(000) = 356$, $T = 291$ K, $R = 0.049$ for 3983 observed reflections. (*Z*)-isomer: monoclinic, $P2_1/c$, $a = 8.653$ (3), $b = 5.762$ (2), $c = 33.365$ (10) Å, $\beta = 83.15$ (3)°, $V = 1651.65$ Å³, $Z = 4$, $D_x = 1.41$, $D_m = 1.39$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.57$ cm⁻¹, $F(000) = 712$, $T = 291$ K, $R = 0.051$ for 1564 observed reflections. Both isomers have a propeller conformation. The vinylic double bond in both isomers is twisted. All aryl rings are planar.

Introduction. Triarylvinyl bromides have been of interest in the study of solvolytic rearrangements of triarylvinyl cations. Structures of 1-anisyl-2,2-diphenylvinyl bromide (Kaftory, Apeloig & Rappoport, 1985) and (*E*)-1,2-dianisyl-2-tolylvinyl bromide

(Wanigasekera, Lee, Houminer, Aviv & Rappoport, 1984) have been recently investigated in association with the solvolytic study. The title compounds were prepared and X-ray structure determinations were carried out as a part of solvolytic rearrangement studies with ¹⁴C- or ¹³C-labeled 1,2-diphenyl-2-(4-tolylvinyl) bromides.

Experimental. Crystals of the title compounds can be prepared either from ordinary deoxybenzoin or from 1,2-diphenylethanone prepared from 90% ¹³C-enriched BaCO₃. The (*Z*)- and (*E*)-isomers were separated by fractional crystallization from 10% acetone-90% methanol at room temperature. A pale yellow crystal of the (*E*)-isomer, with approximate dimensions 0.1 × 0.2 × 0.4 mm, and a colorless crystal of the (*Z*)-isomer, with a cylinder shape of approximate diameter 0.1 mm and height 0.3 mm, were chosen for study. Densities by flotation. All intensity data were collected with a modified Picker four-circle diffractometer with

graphite-monochromated Mo K α radiation, $\theta/2\theta$ scan technique. Three standard reflections were monitored after every 47 reflections during data collection for each compound. There were no significant changes in the intensity of all standard reflections.

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
(E)-isomer (I)				
Br	-0.08701 (3)	0.47618 (6)	0.85947 (6)	6.51 (6)
C(1)	0.0173 (3)	0.4887 (5)	0.7654 (5)	4.7 (4)
C(2)	0.0353 (3)	0.6174 (5)	0.7129 (5)	4.2 (4)
C(3)	0.0676 (3)	0.3468 (5)	0.7560 (4)	4.1 (4)
C(4)	0.0394 (3)	0.2370 (6)	0.7271 (5)	5.3 (5)
C(5)	0.0883 (4)	0.1081 (6)	0.7155 (5)	5.5 (5)
C(6)	0.1660 (3)	0.0851 (6)	0.7339 (5)	5.1 (5)
C(7)	0.1958 (3)	0.1917 (6)	0.7648 (5)	5.0 (5)
C(8)	0.1466 (3)	0.3213 (5)	0.7770 (5)	4.6 (5)
C(9)	0.1115 (3)	0.6352 (5)	0.6209 (5)	3.9 (4)
C(10)	0.1285 (3)	0.5855 (5)	0.5036 (5)	4.6 (5)
C(11)	0.1967 (3)	0.6098 (6)	0.4187 (5)	5.5 (5)
C(12)	0.2495 (3)	0.6814 (6)	0.4452 (5)	5.4 (5)
C(13)	0.2328 (3)	0.7287 (6)	0.5625 (5)	5.4 (5)
C(14)	0.1645 (3)	0.7072 (6)	0.6466 (5)	4.7 (5)
C(15)	0.3230 (3)	0.7099 (7)	0.3505 (6)	8.1 (7)
C(16)	-0.0161 (3)	0.7545 (5)	0.7355 (5)	3.9 (4)
C(17)	-0.0459 (3)	0.8539 (6)	0.6303 (5)	5.0 (5)
C(18)	-0.0919 (3)	0.9844 (6)	0.6484 (5)	5.4 (5)
C(19)	-0.1070 (3)	1.0714 (6)	0.7698 (6)	5.8 (5)
C(20)	-0.0777 (3)	0.9195 (7)	0.8741 (6)	6.4 (6)
C(21)	-0.0321 (3)	0.7887 (6)	0.8581 (5)	5.4 (5)
(E)-isomer (II)				
Br	0.54565 (3)	0.40330 (6)	0.35761 (5)	5.77 (6)
C(1)	0.6023 (3)	0.4625 (6)	0.1848 (4)	4.2 (4)
C(2)	0.6011 (3)	0.6001 (5)	0.1324 (4)	3.9 (4)
C(3)	0.6452 (3)	0.3372 (5)	0.1269 (4)	3.8 (4)
C(4)	0.6098 (3)	0.2244 (5)	0.1280 (5)	4.9 (5)
C(5)	0.6490 (3)	0.1124 (5)	0.0688 (5)	4.9 (5)
C(6)	0.7257 (3)	0.1122 (6)	0.0103 (5)	5.2 (5)
C(7)	0.7639 (3)	0.2217 (6)	0.0114 (5)	5.1 (5)
C(8)	0.7241 (3)	0.3328 (5)	0.0701 (5)	4.5 (5)
C(9)	0.6366 (3)	0.6474 (5)	-0.0072 (5)	3.7 (4)
C(10)	0.6121 (3)	0.6124 (5)	-0.1109 (5)	4.4 (5)
C(11)	0.6451 (3)	0.6603 (6)	-0.2398 (5)	5.0 (5)
C(12)	0.7045 (3)	0.7414 (6)	-0.2683 (5)	5.0 (5)
C(13)	0.7288 (3)	0.7763 (6)	-0.1657 (5)	5.2 (5)
C(14)	0.6950 (3)	0.7326 (5)	-0.0368 (5)	4.7 (5)
C(15)	0.7399 (4)	0.7916 (7)	-0.4084 (5)	8.0 (7)
C(16)	0.5640 (3)	0.7188 (5)	0.2029 (5)	3.9 (4)
C(17)	0.5058 (3)	0.8261 (6)	0.1505 (5)	5.0 (5)
C(18)	0.4722 (3)	0.9387 (6)	0.2114 (6)	6.3 (6)
C(19)	0.4972 (4)	0.9464 (7)	0.3247 (7)	7.0 (7)
C(20)	0.5557 (4)	0.8434 (7)	0.3760 (6)	7.2 (7)
C(21)	0.5898 (3)	0.7282 (6)	0.3171 (5)	5.5 (5)
(Z)-isomer				
Br	-0.00622 (9)	0.32078 (17)	0.05101 (2)	6.57 (6)
C(1)	0.0071 (7)	0.3114 (13)	0.1088 (2)	4.5 (4)
C(2)	0.1336 (7)	0.2341 (11)	0.1217 (2)	3.6 (4)
C(3)	-0.1432 (7)	0.3884 (13)	0.1320 (2)	3.6 (5)
C(4)	-0.2157 (9)	0.5923 (15)	0.1246 (2)	4.7 (5)
C(5)	-0.3575 (8)	0.6516 (15)	0.1467 (2)	5.4 (6)
C(6)	-0.4249 (8)	0.5016 (16)	0.1761 (2)	5.2 (6)
C(7)	-0.3542 (8)	0.3002 (15)	0.1834 (2)	5.3 (6)
C(8)	-0.2129 (7)	0.2398 (12)	0.1614 (2)	4.6 (5)
C(9)	0.1592 (7)	0.2547 (12)	0.1656 (2)	3.6 (5)
C(10)	0.1148 (7)	0.4501 (13)	0.1881 (2)	4.3 (5)
C(11)	0.1445 (8)	0.4645 (15)	0.2282 (2)	5.1 (6)
C(12)	0.2148 (8)	0.2877 (16)	0.2456 (2)	5.3 (6)
C(13)	0.2589 (8)	0.0903 (14)	0.2239 (2)	5.2 (6)
C(14)	0.2307 (7)	0.0712 (13)	0.1839 (2)	4.5 (5)
C(15)	0.2643 (7)	0.1177 (12)	0.0958 (2)	3.7 (5)
C(16)	0.4141 (7)	0.2075 (13)	0.0920 (2)	4.1 (5)
C(17)	0.5343 (7)	0.0906 (15)	0.0694 (2)	5.2 (6)
C(18)	0.5102 (9)	-0.1202 (13)	0.0507 (2)	4.6 (5)
C(19)	0.3614 (8)	-0.2055 (14)	0.0550 (2)	5.4 (6)
C(20)	0.2400 (8)	-0.0928 (13)	0.0767 (2)	5.1 (6)
C(21)	0.6441 (8)	-0.2434 (13)	0.0266 (2)	7.2 (6)

(E)-isomer. Cell parameters obtained from the least-squares refinement of the positions of 32 reflections in the range $30 < 2\theta < 40^\circ$. Intensity data collected in the 2θ range $3-50^\circ$ with $-19 \leq h \leq 20$, $0 \leq k \leq 11$, $-11 \leq l \leq 12$. A total of 5965 independent reflections collected, of which 3983 were considered as

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

	(E)-isomer		(Z)-isomer
	(I)	(II)	
Br-C(1)	1.924 (5)	1.931 (4)	1.946 (10)
C(1)-C(2)	1.324 (7)	1.319 (7)	1.302 (9)
C(1)-C(3)	1.487 (7)	1.496 (7)	1.498 (9)
C(3)-C(4)	1.388 (9)	1.371 (8)	1.371 (11)
C(4)-C(5)	1.379 (8)	1.383 (7)	1.397 (9)
C(5)-C(6)	1.368 (9)	1.370 (7)	1.384 (11)
C(6)-C(7)	1.386 (9)	1.380 (9)	1.347 (12)
C(7)-C(8)	1.388 (7)	1.376 (8)	1.393 (9)
C(8)-C(3)	1.396 (7)	1.396 (7)	1.383 (9)
C(2)-C(9)	1.515 (7)	1.496 (6)	1.512 (10)
C(9)-C(10)	1.401 (8)	1.385 (9)	1.382 (10)
C(10)-C(11)	1.383 (7)	1.389 (7)	1.395 (10)
C(11)-C(12)	1.372 (9)	1.385 (8)	1.352 (12)
C(12)-C(13)	1.389 (8)	1.372 (9)	1.378 (11)
C(12)-C(15)	1.510 (7)	1.504 (7)	
C(13)-C(14)	1.375 (7)	1.386 (7)	1.389 (10)
C(14)-C(9)	1.374 (9)	1.397 (8)	1.401 (10)
C(2)-C(16)	1.488 (7)	1.498 (7)	
C(16)-C(17)	1.383 (7)	1.377 (7)	1.385 (9)
C(17)-C(18)	1.388 (8)	1.378 (8)	1.393 (11)
C(18)-C(19)	1.366 (9)	1.370 (11)	1.370 (10)
C(19)-C(20)	1.367 (8)	1.356 (9)	1.367 (10)
C(20)-C(21)	1.383 (8)	1.388 (9)	
C(21)-C(16)	1.382 (8)	1.392 (8)	
C(2)-C(15)			1.498 (9)
C(15)-C(16)			1.387 (9)
C(20)-C(15)			1.398 (10)
C(18)-C(21)			1.507 (10)
Br-C(1)-C(2)	118.6 (4)	120.2 (4)	119.3 (5)
Br-C(1)-C(3)	113.7 (3)	112.1 (3)	110.7 (5)
C(2)-C(1)-C(3)	127.6 (5)	127.6 (4)	130.0 (6)
C(1)-C(2)-C(9)	121.2 (4)	120.4 (4)	121.3 (6)
C(1)-C(2)-C(16)	124.3 (4)	124.3 (4)	
C(1)-C(2)-C(15)			124.7 (6)
C(9)-C(2)-C(16)	114.5 (4)	115.2 (4)	
C(9)-C(2)-C(15)			114.0 (5)
C(1)-C(3)-C(4)	122.8 (5)	122.2 (4)	123.2 (6)
C(1)-C(3)-C(8)	119.3 (5)	119.7 (5)	117.6 (6)
C(4)-C(3)-C(8)	117.9 (4)	118.1 (4)	119.2 (6)
C(3)-C(4)-C(5)	121.2 (5)	121.6 (5)	120.5 (7)
C(4)-C(5)-C(6)	120.4 (6)	119.3 (5)	119.3 (8)
C(5)-C(6)-C(7)	119.9 (5)	120.5 (5)	120.3 (6)
C(6)-C(7)-C(8)	119.8 (5)	119.6 (5)	120.6 (7)
C(3)-C(8)-C(7)	120.7 (5)	120.8 (5)	120.1 (7)
C(2)-C(9)-C(10)	121.3 (5)	122.0 (5)	121.8 (6)
C(2)-C(9)-C(14)	121.0 (5)	120.1 (5)	119.1 (6)
C(10)-C(9)-C(14)	117.6 (5)	117.8 (4)	119.1 (6)
C(9)-C(10)-C(11)	119.8 (6)	120.7 (5)	119.9 (7)
C(10)-C(11)-C(12)	122.2 (5)	121.2 (6)	120.7 (7)
C(11)-C(12)-C(13)	117.7 (5)	118.1 (5)	120.5 (7)
C(11)-C(12)-C(15)	121.8 (5)	120.5 (6)	
C(13)-C(12)-C(15)	120.6 (6)	121.4 (5)	
C(12)-C(13)-C(14)	120.6 (6)	121.4 (5)	120.1 (7)
C(13)-C(14)-C(9)	122.0 (5)	120.7 (6)	119.7 (7)
C(2)-C(15)-C(16)			121.2 (6)
C(2)-C(15)-C(20)			120.5 (6)
C(16)-C(15)-C(20)			118.1 (6)
C(2)-C(16)-C(17)	119.5 (5)	119.7 (5)	
C(2)-C(16)-C(21)	121.8 (4)	121.6 (4)	
C(17)-C(16)-C(21)	118.7 (5)	118.6 (5)	
C(15)-C(16)-C(17)			120.1 (7)
C(16)-C(17)-C(18)	120.4 (5)	120.9 (5)	121.7 (6)
C(17)-C(18)-C(19)	120.4 (5)	120.2 (5)	117.1 (6)
C(17)-C(18)-C(21)			120.2 (6)
C(19)-C(18)-C(21)			122.7 (7)
C(18)-C(19)-C(20)	119.4 (5)	119.7 (6)	122.6 (7)
C(19)-C(20)-C(21)	121.0 (6)	121.1 (7)	
C(19)-C(20)-C(15)			120.4 (6)
C(20)-C(21)-C(16)	120.1 (5)	119.5 (5)	

Table 3. Relevant torsional angles ($^{\circ}$) with *e.s.d.*'s in parentheses

	Absolute values are listed.		(Z)-isomer
	(I)	(II)	
	(E)-isomer		
C(3)–C(1)–C(2)–C(9)	6.1 (9)	8.6 (9)	13 (1)
C(1)–C(2)–C(9)–C(10)	59.2 (7)	57.2 (7)	39.1 (9)
C(2)–C(1)–C(3)–C(8)	46.2 (8)	46.3 (8)	51 (1)
C(1)–C(2)–C(16)–C(17)	65.6 (9)	60.6 (8)	
C(1)–C(2)–C(15)–C(16)			63 (1)

observed with $I > 2\sigma(I)$. Lorentz, polarization and absorption corrections applied (transmission factors 0.910–0.955). Br atoms located from Patterson map. Subsequent difference Fourier syntheses gave all non-H atoms. After several cycles of full-matrix least-squares anisotropic refinement (on F), all H atoms were calculated at the idealized positions based on the molecular geometry with C–H = 1.00 Å. These positions were constrained during the subsequent refinement. In final cycles of refinement, thermal parameters for all H atoms were constrained to the equivalent isotropic temperature factor of the C atoms to which they were bonded. Final $R = 0.049$ and $wR = 0.049$ with $w = 1/\sigma^2(F)$. $S = 1.22$, $(\Delta/\sigma)_{\max} = 0.0005$, max. electron density found in the final difference Fourier syntheses $0.78 \text{ e } \text{Å}^{-3}$, at a position 1.07 Å from the Br atom.

(Z)-isomer. Cell parameters from 18 reflections in the range $29 < 2\theta < 39^{\circ}$. Intensity data collected in the 2θ range $3\text{--}45^{\circ}$ with $0 \leq h \leq 9$, $0 \leq k \leq 6$, $-35 \leq l \leq 35$. A total of 2166 independent reflections collected, of which 1564 reflections were considered as observed with $I > 2\sigma(I)$. Lorentz–polarization corrections applied. No absorption correction applied. Direct methods using *XTAL* system of crystallographic programs (Stewart & Hall, 1984) gave all non-H atoms. The treatment of H atoms and refinements were the same as for the (E)-isomer. Final $R = 0.051$ and $wR = 0.046$ with $w = 1/\sigma^2(F)$. $S = 2.3$, $(\Delta/\sigma)_{\max} = 0.0005$, max. electron density found in the final difference Fourier synthesis $0.77 \text{ e } \text{Å}^{-3}$, at a position 1.85 Å from the Br atom.

Atomic scattering factors for both structure determinations were from Cromer & Mann (1968). All computations were carried out with a VAX8600 computer and the *XTAL* system of crystallographic programs.

Discussion. Table 1 lists the fractional atomic coordinates.* Bond lengths and angles are given in Table 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43238 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Relevant torsional angles are listed in Table 3. *ORTEP* (Johnson, 1965) views of the molecules are given in Figs. 1 and 2 respectively.

The pale yellow compound with the lower melting point is the (E)-isomer and was designated as such in the solvolytic study (Lee & Wanigasekera, 1986). In the (E)-isomer, there are two crystallographically independent but chemically equivalent molecules present in the asymmetric unit, the maximum differences in equivalent bond lengths and angles in the two molecules being 0.023 Å and 1.6° respectively. The shortest intermolecular distance [$2.543 (7) \text{ Å}$] is between H(19) in molecule (I) and H(6) in molecule (II). Torsional

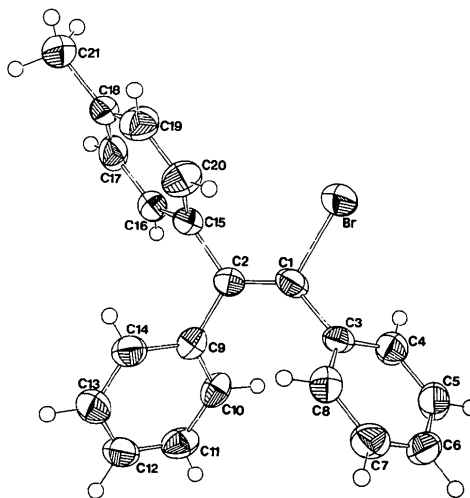


Fig. 1. *ORTEP* (Johnson, 1965) view of the (Z)-isomer with thermal ellipsoids drawn at the 50% probability level.

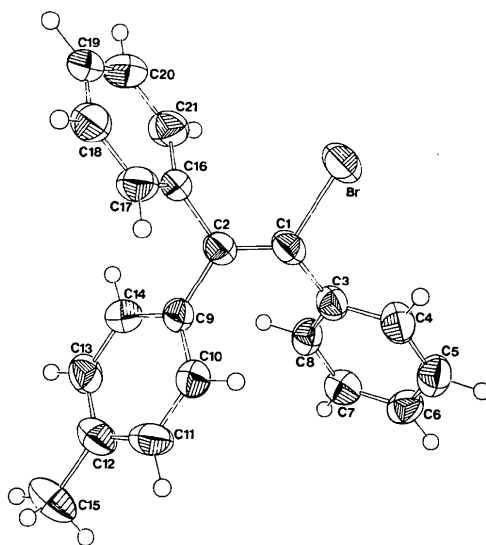


Fig. 2. *ORTEP* (Johnson, 1965) view of the (E)-isomer with thermal ellipsoids drawn at the 50% probability level.

angles C(3)–C(1)–C(2)–C(9) of $6.1(9)^\circ$ in (I) and $8.6(9)^\circ$ in (II) indicate that the C=C double bonds are twisted. All aryl rings are planar and rotated in the same sense from the plane of the central double bond to form a propeller conformation which minimizes the steric interaction between neighbouring aryl groups. Although both molecules adopt similar conformations, the torsional angle C(1)–C(2)–C(16)–C(21) of $65.6(8)^\circ$ in molecule (I) is significantly different from that of $60.6(8)^\circ$ in molecule (II), which indicates that packing forces affect the molecular conformation to some degree. The Br–C bond lengths of 1.924 (5) and 1.931 (4) Å are significantly longer than the reported mean value of 1.888 Å for Br–C bonds in other olefinic compounds (Kaftory, Apeloig & Rappoport, 1985), but they are similar to those in other triarylvinyl bromides. Other bond lengths and bond angles are in agreement with those reported for other triarylvinyl bromides (Wanigasekera *et al.*, 1984; Kaftory, Biali & Rappoport, 1985).

All aryl rings are also planar in the (Z)-isomer and the molecule adopts a conformation similar to that of the (E)-isomer. The torsional angles C(2)–C(1)–C(3)–C(8), C(1)–C(2)–C(9)–C(10) and C(1)–C(2)–C(15)–C(20) are $51(1)$, $39.1(9)$ and $63(1)^\circ$ respectively, which are within the range 38.3 – 79.0° for a series of triarylvinyl propellers reported by Kaftory, Biali & Rappoport (1985). Although the torsional angle equivalent to C(1)–C(2)–C(9)–C(10) has been found to be smaller (38.3°) in (Z)-1,2-dimesityl-2-phenylethenol, the torsional angles equivalent to C(2)–C(1)–C(3)–C(8) and C(1)–C(2)–C(15)–C(20) are 79.0 and 74.4° in that compound. The small value of the C(1)–C(2)–C(9)–C(10) torsional angle increases the steric repulsive interaction between the α - and β -aryl groups. Hence the central C=C bond is twisted more severely. The C(3)–C(1)–C(2)–C(9)

torsional angle of $13(1)^\circ$ is not only larger than that of 1.1° in (Z)-1,2-dimesityl-2-phenylethenol but also than in the (E)-isomer and in other triarylvinyl compounds (Luo, Barton, Robertson, Lee & Wanigasekera, 1986; Kaftory, Biali & Rappoport, 1985; Biali & Rappoport, 1984). The unusually short C=C bond and the related long Br–C bond may be partly due to a spurious error in the position of atom C(1). It would be necessary to change the coordinates of atom C(1) by approximately three times their estimated standard deviations in order to give C=C and C–Br bond lengths similar to those in the (E)-isomer. Other bond lengths and bond angles are normal.

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Structure of a Four-Fused-Ring System Obtained by Intramolecular [2 + 2] Photoaddition

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Abstract. 9,9-Dimethyl-3-oxatetracyclo[5.5.1.0^{1,8}.-0^{4,13}]tridecan-6-one, C₁₄H₂₀O₂, *M_r* = 220.31, monoclinic, *P*2₁/*c*, *a* = 15.342 (2), *b* = 6.593 (1), *c* =

13.085 (2) Å, β = $113.71(1)^\circ$, *V* = 1211.8 (3) Å³, *Z* = 4, *D_m* = 1.18, *D_x* = 1.208 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71069 Å, μ = 0.073 mm⁻¹, *F*(000) = 480, room tem-