with bond angles are in Table 2.* Fig. 1 (Motherwell & Clegg, 1978) shows the stereochemical arrangement of the BBDT-TTF molecule. In the molecule, the $C_6S_8$ core is highly planar; the maximum deviation being for S(4) [0.039 (5) Å out of the least-squares plane]. An analogous tetrathiafulvalene compound ($TTC_8$-TTF) reported recently (Nakano, Imaeda, Mori, Maruyama, Inokuchi, Iwasawa & Saito, 1991) also has a planar $C_6S_8$ core. In the eight-membered exterior ring, atoms S(3), S(4), C(3) and C(6) form a plane (plane 1) within deviations of ±0.039 (5) Å whereas C(4) and C(5) are out of this plane by 0.612 (4) and −0.335 (3) Å respectively. The dihedral angle between the core plane and plane 1 is 78.9 (3)°. The molecules are stacked uniformly as parallel 'Z'-shaped arrays along the *a* axis (Fig. 2). The core planes are inclined to the axis by approximately 45° (66° in the case of BMDT-TTF; Kato, Kobayashi, Kobayashi & Sasaki, 1985). Average C($sp^3$)—S and C($sp^2$)—S distances are 1.819 (3) and 1.753 (2) Å respectively. Important structural parameters for BBDT-TTF are listed in Table 3 along with those for the analogous sulfur-containing π donors BMDT-TTF, BEDT-TTF (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986) and BPDT-TTF (Porter, Kini & Williams, 1987). Similar to BEDT-TTF, BBDT-TTF molecules are arranged in pairs in the crystal (Fig. 3). Three intermolecular S···S distances are close to twice the van der Waals radius of sulfur, 3.70 Å. These distances are $S2\cdots S2^{i} = 3.686\,(1)$, $S1\cdots S4^{ii} = 3.668\,(1)$ and $S3\cdots S4^{iii} = 3.705\,(1)$ Å [(i) $2-x$, $1-y$, $-z$; (ii) $-1+x$, $y$, $z$; (iii) $-1+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$] shown in Figs. 2 and 3 respectively. Electrochemical preparations of the cation-radical salts of BBDT-TTF are in progress.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54518 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Front Strain in the Structure of 2-Benzylidene-1,1,3,3-tetramethylindan, a Sterically Congested Styrene*

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**Abstract.** $C_{20}H_{22}$, $M_r = 262.4$, monoclinic, $P2_1/c$, $a = 8.331\,(3)$, $b = 21.731\,(6)$, $c = 8.804\,(3)$ Å, $\beta = 95.61\,(2)°$, $V = 1586$ Å$^3$, $Z = 4$, $D_x = 1.099$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.057$ mm$^{-1}$, $F(000) = 568$, $T = 294\,(1)$ K, $R = 0.047$, $wR = 0.046$ for 2274 observed reflections. The title compound carries a planar phenyl substituent in an orthogonal relationship to the C=C double bond. Front strain along this double bond is relieved mainly by expansion of two olefinic angles.

**Introduction.** The β,β-di-*tert*-alkyl-substituted 2-benzylidene-1,1,3,3-tetramethylindan (1) was pre-

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* Sterically Congested Molecules, 3. Part 2: Knorr & Polborn (1991).

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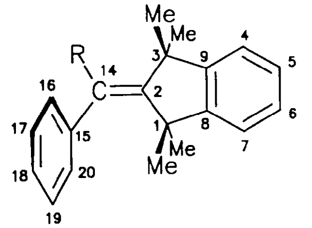
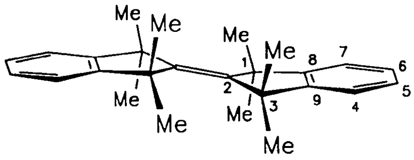
pared by the known procedure (Knorr, Lattke & Räpple, 1980) and was deposited as single crystals from methanol solution. Its structure was needed for a comparison with the corresponding lithium derivative (2) (Knorr, Hoang, Nöth & Linti, 1991) whose crystal structure revealed coordination of Li to the phenyl ring. Although *MM2/π* force-field (Allinger, 1977; Allinger & Yuh, 1983) calculations on (1) predicted a tendency for rotation of the phenyl ring into conjugation with the C=C double bond, we sought experimental evidence for the phenyl conformation when the smaller H atom was the substituent *R*. Furthermore, structural details of (1) appeared to be of interest in relation to the structure (Pilati & Simonetta, 1984) of (3) which exhibited features of strong front strain along the C=C double bond.



(1) $R = \mathrm{H}$
(2) $R = \mathrm{Li}$



(3)

**Experimental.** A colourless transparent rod-shaped crystal (0.2 × 0.3 × 0.5 mm) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters determined from 25 reflections in the range $10 < \theta < 15°$. Lp corrections applied, absorption ignored. Intensities were collected in the range $2 < \theta < 25°$. Range of *hkl*: $-9 \leq h \leq 9$, $0 \leq k \leq 25$, $0 \leq l \leq 10$. Three standard reflections measured every 100 reflections showed intensity variations from 0.9863 to 1.0019. $\omega$-scan technique. Total of 3066 reflections collected, 2604 unique, 2274 observed with $F(hkl) > 4\sigma(F)$, 126 unobserved with $I \leq 0$. Structure solved by direct methods, full-matrix least-squares refinement on $F$ of 181 parameters (*SHELXS*86, Sheldrick, 1986; *SHELXTL-Plus*, Sheldrick, 1987) by minimizing $\sum w(F_o - F_c)^2$, $w^{-1} = \sigma^2(F_o)$. Coordinates and anisotropic displacement parameters refined for non-H atoms. H atoms located 0.96 Å from adjacent non-H atoms and refined in riding mode with fixed isotropic $U = 0.08$ Å$^2$. Final $R = 0.0465$, $wR = 0.0459$ on observed data, $S = 5.09$, $(\Delta/\sigma)_{\max} = 0.001$, $(\Delta\rho)_{\max} = 0.13$, $(\Delta\rho)_{\min} = -0.17$ e Å$^{-3}$, atomic scattering factors as incorporated in the *SHELXTL-Plus* program.

Table 1. *Fractional coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (1) *with e.s.d.'s in parentheses*

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 0.5395 (2) | 0.5908 (1) | 0.2326 (2) | 0.055 (1) |
| C(2) | 0.6613 (2) | 0.5979 (1) | 0.3749 (2) | 0.051 (1) |
| C(3) | 0.6252 (2) | 0.6565 (1) | 0.4621 (2) | 0.057 (1) |
| C(4) | 0.3604 (2) | 0.7212 (1) | 0.4304 (3) | 0.070 (1) |
| C(5) | 0.2118 (3) | 0.7292 (1) | 0.3495 (3) | 0.080 (1) |
| C(6) | 0.1629 (3) | 0.6921 (1) | 0.2265 (3) | 0.080 (1) |
| C(7) | 0.2629 (2) | 0.6465 (1) | 0.1812 (2) | 0.069 (1) |
| C(8) | 0.4127 (2) | 0.6382 (1) | 0.2628 (2) | 0.056 (1) |
| C(9) | 0.4606 (2) | 0.6748 (1) | 0.3871 (2) | 0.056 (1) |
| C(10) | 0.4654 (3) | 0.5266 (1) | 0.2146 (3) | 0.072 (1) |
| C(11) | 0.6164 (3) | 0.6078 (1) | 0.0859 (2) | 0.076 (1) |
| C(12) | 0.7511 (2) | 0.7063 (1) | 0.4389 (3) | 0.082 (1) |
| C(13) | 0.6189 (2) | 0.6452 (1) | 0.6341 (2) | 0.072 (1) |
| C(14) | 0.7825 (2) | 0.5609 (1) | 0.4209 (2) | 0.060 (1) |
| C(15) | 0.8380 (2) | 0.5046 (1) | 0.3470 (2) | 0.056 (1) |
| C(16) | 0.9492 (2) | 0.5085 (1) | 0.2403 (2) | 0.065 (1) |
| C(17) | 1.0031 (3) | 0.4558 (1) | 0.1730 (2) | 0.072 (1) |
| C(18) | 0.9484 (2) | 0.3994 (1) | 0.2096 (2) | 0.068 (1) |
| C(19) | 0.8409 (2) | 0.3946 (1) | 0.3189 (3) | 0.073 (1) |
| C(20) | 0.7879 (2) | 0.4469 (1) | 0.3871 (3) | 0.069 (1) |

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (1) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1.541 (3) | C(5)—C(6) | 1.379 (3) |
| C(1)—C(8) | 1.516 (3) | C(6)—C(7) | 1.379 (3) |
| C(1)—C(10) | 1.528 (3) | C(7)—C(8) | 1.390 (3) |
| C(1)—C(11) | 1.542 (3) | C(8)—C(9) | 1.381 (3) |
| C(2)—C(3) | 1.533 (3) | C(14)—C(15) | 1.481 (3) |
| C(2)—C(14) | 1.322 (2) | C(15)—C(16) | 1.385 (3) |
| C(3)—C(9) | 1.515 (3) | C(15)—C(20) | 1.378 (3) |
| C(3)—C(12) | 1.535 (3) | C(16)—C(17) | 1.384 (3) |
| C(3)—C(13) | 1.540 (3) | C(17)—C(18) | 1.358 (3) |
| C(4)—C(5) | 1.378 (3) | C(18)—C(19) | 1.381 (3) |
| C(4)—C(9) | 1.385 (3) | C(19)—C(20) | 1.379 (3) |

| | | | |
|---|---|---|---|
| C(2)—C(1)—C(8) | 101.8 (1) | C(5)—C(6)—C(7) | 120.5 (2) |
| C(2)—C(1)—C(10) | 113.7 (2) | C(6)—C(7)—C(8) | 118.8 (2) |
| C(8)—C(1)—C(10) | 110.9 (2) | C(1)—C(8)—C(7) | 127.1 (2) |
| C(2)—C(1)—C(11) | 111.3 (1) | C(1)—C(8)—C(9) | 112.2 (1) |
| C(8)—C(1)—C(11) | 109.8 (2) | C(7)—C(8)—C(9) | 120.7 (2) |
| C(10)—C(1)—C(11) | 109.2 (2) | C(3)—C(9)—C(4) | 127.9 (2) |
| C(1)—C(2)—C(3) | 110.1 (1) | C(3)—C(9)—C(8) | 111.9 (2) |
| C(1)—C(2)—C(14) | 127.7 (2) | C(4)—C(9)—C(8) | 120.2 (2) |
| C(3)—C(2)—C(14) | 122.2 (2) | C(2)—C(14)—C(15) | 129.0 (2) |
| C(2)—C(3)—C(9) | 102.3 (1) | C(14)—C(15)—C(16) | 120.3 (2) |
| C(2)—C(3)—C(12) | 110.5 (2) | C(14)—C(15)—C(20) | 121.6 (2) |
| C(9)—C(3)—C(12) | 111.0 (2) | C(16)—C(15)—C(20) | 118.0 (2) |
| C(2)—C(3)—C(13) | 112.8 (2) | C(15)—C(16)—C(17) | 120.4 (2) |
| C(9)—C(3)—C(13) | 110.7 (2) | C(16)—C(17)—C(18) | 121.0 (2) |
| C(12)—C(3)—C(13) | 109.4 (2) | C(17)—C(18)—C(19) | 119.3 (2) |
| C(5)—C(4)—C(9) | 119.0 (2) | C(18)—C(19)—C(20) | 119.9 (2) |
| C(4)—C(5)—C(6) | 120.9 (2) | C(15)—C(20)—C(19) | 121.4 (2) |

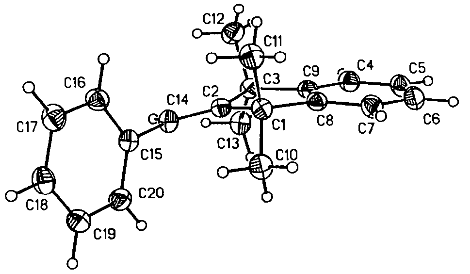


Fig. 1. View of the title compound with 20% thermal ellipsoids.

**Discussion.** Final atomic positional and isotropic displacement parameters for non-H atoms are shown in Table 1.* The rather rigid 1,1,3,3-tetramethyl-2-indanylidene moiety of (1) in Fig. 1 is folded by 13.6° across the C(1)—C(3) axis, much less than in (3). The C(2)—C(14) double bond is short (Table 2) and twisted by 3°. The bonds radiating from C(2) are coplanar but the valency angles at C(2) are strongly distorted, as is C(2)—C(14)—C(15) = 129.0 (2)°. However, the C(2)—Ph distance is normal for a single bond. Therefore, C(2) appears to be angularly rather soft in comparison with an N atom in corresponding C═N double bonds (Knorr, Dietrich & Mahdi, 1991; Knorr & Polborn, 1991) where none of the C—N—C angles exceeded 125°.

The phenyl group is almost orthogonal to the C═C double bond [averaged torsion angles 86.5° about C(14)—C(15)]. It is also practically planar (mean deviation 0.01 Å) despite its several contacts with the opposing *tert*-alkyl system: C(1)—C(15) = 3.197, C(10)—C(15) = 3.242 and C(10)—C(20) = 3.424 Å. Shorter contacts have been found (Mugnoli & Simonetta, 1976) in the related 2,2-di-*tert*-butyl-1,1-diphenylethylene which cannot widen its olefinic angles sufficiently but responds by twisting about its double bond. This front strain has been largely relieved in (1) by angular expansion at C(1)—C(2)—C(14) = 127.7 (2) and C(2)—C(14)—C(15) = 129.0 (2)°, in accord with the normal (for cyclopentylidene moieties) angular value of C(1)—C(2)—C(3) = 110.1 (1)° and the lack of back-bending of the four methyl groups [average angle C(methyl)—C(quaternary)—C(aromatic) = 110.6°]. The latter angles were all much more compressed in (3).

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, torsion angles, intermolecular distances and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54487 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0272]

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# *N*-Ethoxycarbonyl-substituierter Phosphor-Hydrazin-Heterocyclus mit Twist-Konformation

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(*Eingegangen am* 4. *April* 1991; *angenommen am* 11. *Juli* 1991)

**Abstract.** Diethyl 2,4-dimethyl-6-oxo-3-phenoxy-3-thioxo-1,2,4,5-tetraaza-3$\lambda^5$-phosphacyclohexane-1,5-dicarboxylate, $C_{15}H_{21}N_4O_6PS$, $M_r = 416.393$, triclinic, $P\bar{1}$, $a = 7.242$ (1), $b = 11.337$ (2), $c = 12.951$ (3) Å, $\alpha = 73.79$ (2), $\beta = 85.11$ (2), $\gamma = 79.58$ (2)°, $V = 1003.5$ (3) Å$^3$, $Z = 2$, $D_x = 1.378$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.27$ mm$^{-1}$, $F(000) = 436$, $T = 293$ K, $R = 0.057$, $wR = 0.034$ for 3407 unique contributing reflections. The compound was synthesized in our laboratory for a comparison of its ring conformation with those of other 1,2,4,5-tetraaza-3$\lambda^5$-phosphacyclohexanes. The saturated six-membered ring adopts a twist conformation, torsion angles: PNNC −62.7 (3) and −68.2 (3), NPNN 33.5 (2) and 24.4 (2), NCNN 32.7 (2)°. The substituents at P are in equiclinal positions. Bond distances: N—N 1.407 (3) and 1.396 (3), P—S 1.899 (1), P—O 1.583 (3), P—N

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