

the vapor treatment to the crystal parameters obtained here for modifications (I) and (II). However, neither of these modifications coincides with that of the photoactive phase caused by the vapor treatment.

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References

FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 1.1. Enraf-Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

IQBAL, A., CASSAR, L., ROCHAT, A. C., PFENNINGER, J. & WALLQUIST, O. (1988). *J. Coat. Tech.* **60**, 37–45.

JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MIZUGUCHI, J. (1981). *Krist. Tech.* **16**, 695–700.

MIZUGUCHI, J. & HOMMA, S. (1989). *J. Appl. Phys.* **66**, 3104–3110.

MIZUGUCHI, J. & ROCHAT, A. C. (1988). *J. Imag. Sci.* **132**, 135–140.

PAULING, L. (1960). *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, ch. 12. Cornell Univ. Press.

Acta Cryst. (1990). **C46**, 1903–1906

Structure of *trans*-2 β -(4-Chlorophenyl)-1,3-dithiadecalin

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Abstract. 3-(4-Chlorophenyl)-2,4-dithiabicyclo[4.4.0]decane, $C_{14}H_{17}ClS_2$, $M_r = 284.9$, monoclinic, $P2_1/n$, $a = 6.774$ (1), $b = 24.307$ (2), $c = 8.864$ (1) Å, $\beta = 108.78$ (1)°, $V = 1381.8$ (3) Å³, $Z = 4$, $D_m = 1.36$ (floatation in aqueous KI solution), $D_x = 1.369$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 5.06$ mm⁻¹, $F(000) = 600$, $T = 291$ K, final $R = 0.049$ ($wR = 0.050$) for 1554 observed reflections. Both the cyclohexane and the dithiane ring of the bicyclic system have chair conformations. The equatorially attached phenyl ring is nearly eclipsed with respect to one of the C—S bonds of the dithiane ring with a corresponding torsion angle S—C(dithiane)—C(phenyl)—C(phenyl) of -14.6 (6)°.

Introduction. This study is part of a series of structural investigations on the crystalline phases of mesogenic materials. The title compound itself does not form mesomorphic phases, but serves as a model structure for conformational analysis of a new class of liquid-crystalline heteroalicyclic substances containing the 2-(4-substituted phenyl)-1,3-dithiadecalin moiety (Tschierske, Joachimi, Vorbrodt, Zäschke, Wiegeleben, Hauser & Demus, 1989). The X-ray

crystal structure analysis reported in this paper was performed to obtain accurate geometrical parameters of the molecular structure for comparison with NMR measurements and a starting point for theoretical calculations, the results of which will be published elsewhere (Tschierske, Kleinpeter, Köhler & Zäschke, 1990).

Experimental. The title compound was synthesized by Tschierske (Tschierske, Joachimi, Vorbrodt, Zäschke, Wiegeleben, Hauser & Demus, 1989). A colourless optically clear crystal was cut to the dimensions $0.34 \times 0.34 \times 0.13$ mm and mounted on a Syntex $P2_1$ diffractometer. Measurements were carried out with graphite-monochromatized $\text{Cu } K\alpha$ radiation (monochromator angle 26.57°), unit-cell parameters were determined by a least-squares treatment of the setting angles for 15 reflections in the 2θ range $20\text{--}30^\circ$. 1645 unique intensity data were measured for reflections with $2\theta < 115^\circ$ and h, k, l ranging from $-7, 0, 0$ to $7, 26, 9$. The intensities of the check reflections varied by $\pm 1.8\%$ for $\bar{1}42$ and by $\pm 2.1\%$ for $\bar{1}22$. 1558 reflections had intensities $I > 1.96\sigma(I)$ and were considered observed. Lp correction was applied during data reduction.

The structure was solved by direct methods and refined by full-matrix least-squares methods on F with atomic scattering factors from *SHELX76*

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(Sheldrick, 1976). After the refinement with isotropic displacement parameters for non-H atoms and an empirical absorption correction with max. and min. coefficients of 1.279 and 0.844, respectively, was applied using the program *DIFABS* (Walker & Stuart, 1983). Subsequently, the refinement was continued with anisotropic displacement parameters for non-H atoms and geometrically calculated H-atom positions 'riding' on the appropriate C atoms. Weights $w = 1/\sigma^2(F)$ were introduced and four reflections that still had large $F_o - F_c$ differences were excluded from the last cycles of refinement, leading to a final R value of 0.049 ($wR = 0.050$). The maximum shift/ σ value for a parameter during the last cycle was 0.016, 10.1 reflections per parameter were available. A final difference Fourier synthesis showed max. and min. $\Delta\rho$ of 0.24 and -0.46 e \AA^{-3} , respectively.

All calculations were performed on an IBM-XT computer of Poznań University using the above-mentioned programs and those of the *XTL* (Syntex, 1973), *SHELXS86* (Sheldrick, 1986) and *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1986) packages.

Discussion. Table 1 contains the final non-H-atom coordinates and their equivalent isotropic displacement parameters.* The molecular structure is illustrated by an *ORTEP* plot in Fig. 1; selected geometrical bond parameters are summarized in Table 2.

* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52929 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates of non-H atoms and equivalent isotropic displacement factors

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C1	0.1420 (8)	0.4500 (2)	0.3588 (5)	0.048 (2)
C2	0.2751 (8)	0.4060 (2)	0.4114 (5)	0.050 (2)
C3	0.1936 (7)	0.3545 (2)	0.4201 (5)	0.044 (2)
C4	-0.0219 (7)	0.3462 (2)	0.3765 (5)	0.038 (2)
C5	-0.1499 (8)	0.3918 (2)	0.3283 (5)	0.051 (2)
C6	-0.0711 (9)	0.4434 (2)	0.3182 (6)	0.055 (3)
C7	-0.1217 (7)	0.2910 (2)	0.3802 (5)	0.038 (2)
C8	-0.1221 (7)	0.1773 (2)	0.3730 (5)	0.040 (2)
C9	-0.2320 (6)	0.1750 (2)	0.5002 (5)	0.038 (2)
C10	-0.3696 (7)	0.2249 (2)	0.4954 (5)	0.043 (2)
C11	0.0026 (8)	0.1250 (2)	0.3715 (6)	0.051 (2)
C12	-0.1314 (9)	0.0735 (2)	0.3537 (6)	0.060 (3)
C13	-0.2385 (8)	0.0708 (2)	0.4800 (6)	0.054 (2)
C14	-0.3638 (7)	0.1226 (2)	0.4769 (5)	0.048 (2)
S1	0.2417 (3)	0.51486 (5)	0.3407 (2)	0.0737 (7)
S2	0.0582 (2)	0.23443 (4)	0.3978 (2)	0.0426 (4)
S2	-0.2369 (2)	0.29074 (5)	0.5398 (2)	0.0433 (4)

Table 2. Selected bond lengths (Å), angles and torsion angles (°)

C1—C1	1.743 (5)	C9—C10	1.523 (6)
C4—C7	1.506 (6)	C9—C14	1.530 (6)
C7—S1	1.810 (5)	C8—C11	1.529 (7)
C7—S2	1.822 (5)	C11—C12	1.523 (7)
C8—S1	1.816 (5)	C12—C13	1.519 (9)
C10—S2	1.816 (5)	C13—C14	1.513 (7)
C8—C9	1.540 (7)		
C6—C1—C1	119.0 (4)	C8—C9—C10	112.7 (4)
C2—C1—C1	120.1 (4)	C9—C10—S2	116.1 (4)
C3—C4—C7	123.9 (4)	C11—C8—S1	106.6 (3)
C5—C4—C7	118.6 (4)	C10—C9—C14	109.5 (4)
C4—C7—S2	109.1 (3)	C9—C8—C11	112.0 (3)
C4—C7—S1	112.6 (3)	C8—C9—C14	109.3 (4)
C7—S1—C8	99.4 (2)	C8—C11—C12	111.8 (5)
C7—S2—C10	98.1 (2)	C11—C12—C13	111.7 (4)
S1—C7—S2	112.0 (3)	C12—C13—C14	110.4 (4)
C9—C8—S1	113.8 (3)	C9—C14—C13	113.0 (4)
C11—C8—C9—C14	-53.8 (5)	S1—C8—C11—C12	179.1 (4)
C9—C8—C11—C12	54.0 (5)	C10—C9—C14—C13	179.9 (4)
C8—C11—C12—C13	-54.3 (6)	C4—C7—S1—C8	-173.2 (3)
C11—C12—C13—C14	55.1 (6)	C4—C7—S2—C10	172.7 (3)
C12—C13—C14—C9	-57.1 (6)	S2—C7—S1—C8	63.4 (3)
C8—C9—C14—C13	56.0 (5)	C9—C8—S1—C7	-60.4 (4)
C11—C8—S1—C7	175.6 (3)	S1—C8—C9—C10	63.2 (4)
C14—C9—C10—S2	174.4 (3)	C8—C9—C10—S2	-63.8 (5)
C11—C8—C9—C10	-175.8 (4)	C9—C10—S2—C7	59.7 (4)
S1—C8—C9—C14	-174.8 (3)	S1—C7—S2—C10	-62.0 (3)

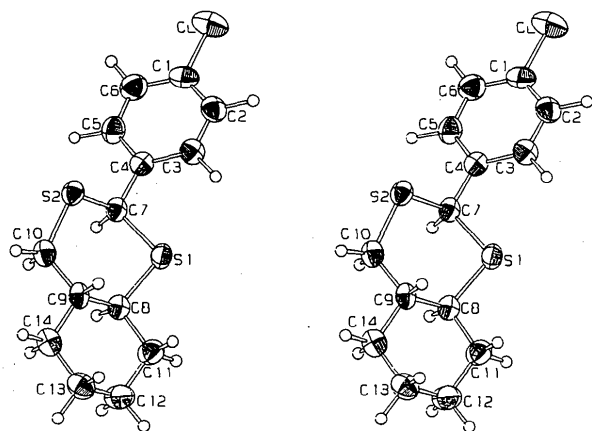


Fig. 1. Stereo *ORTEP* plot (Johnson, 1976) of the molecular structure with atom-labelling scheme (thermal ellipsoids at the 50% probability level, H-atom circles of arbitrary size).

Both six-membered rings of the *trans*-1,3-dithiadecalin moiety adopt a chair conformation in agreement with earlier thermodynamical evaluations of heterocyclic compounds by Zefirov & Kasimirchik (1974), who proved the chair conformation to be the most stable atom arrangement for 1,3-dithiane.

The cyclohexane part of the bicyclic system deviates only very slightly from an ideal chair, mean values of bond lengths, angles and torsion angles being 1.525 (10) Å, 111.4 (13) and 55.1 (13)°, respectively (numbers in parentheses here and below are root-mean squares of individual e.s.d.'s).

All endocyclic geometrical bond parameters for the dithiane ring are listed in Table 2. To our

knowledge no X-ray structure analysis of any compound containing the 1,3-dithiadecalin fragment has been undertaken up to now. On the other hand, several crystal structures with the 1,3-dithiane fragment are known (Bulman-Page, Chadwick, van Niel & Westwood, 1987). Thus a comparison with the phenyl-substituted compounds 2-phenyl-1,3-dithiane (Kalf & Romers, 1966) (1) and 1-methyl-3-(*cis*-2-phenyl-1,3-dithian-5-yl)-2-thiourea (2) and the corresponding *trans* compound (3) (Borgulya, Daly, Schonholzer & Bernauer, 1984) seemed reasonable. An excellent agreement for the endocyclic torsion angles of the title compound [mean value 62.1 (1.7) $^\circ$] with those of (2) [62.1 (1.7) $^\circ$] and (3) [62.4 (1.9) $^\circ$] has been found. Also, the torsion angles of (1) [mean value 58 (4) $^\circ$] are not significantly different considering their rather high standard deviations of about 2.5 $^\circ$. All corresponding bond lengths and angles within the dithiane fragments of the four compounds are also quite similar, *e.g.* the mean C—S distance is 1.816 (6) Å for the title compound and 1.81 (2), 1.816 (7) and 1.812 (5) Å for (1), (2) and (3), respectively. Minor deviations are due to the different kinds of substitution on the ring.

The mutual orientation of the bicyclic system and the equatorially attached phenyl ring may be described by the appropriate torsion angles [values in parentheses are the corresponding torsion angles in (1), (2) and (3), in this sequence]: τ_1 (S1—C7—C4—C3) -14.6 (6) (-66.0, -41.6, -30.7) $^\circ$, τ_2 (S2—C7—C4—C3) 110.4 (5) (59.7, 82.5, 92.7) $^\circ$, τ_3 (S2—C7—C4—C5) -69.1 (5) (-117.5, -95.7, -84.8) $^\circ$, and τ_4 (S1—C7—C4—C5) 165.9 (4) (116.8, 140.2, 151.8) $^\circ$. As already stated by Burkert & Allinger (1982), X-ray investigations and theoretical calculations on phenylcyclohexyl derivatives clearly indicate a coplanar arrangement of the phenyl group and the bisecting mirror plane of the cyclohexane ring (corresponding to $\tau_1 = -60^\circ$) to be the most stable one, the equatorial H atom on the neighbouring C atoms preventing very different geometries. In 2-phenyl-1,3-dioxane, on the other hand, there are no H atoms in positions 1 and 3, hence a very low barrier of rotation about the dioxane-phenyl bond

has been calculated and no preferred orientation has been found in crystals of its derivatives (Burkert & Allinger, 1982). From this point of view 2-phenyl-1,3-dithiane derivatives are comparable to the dioxane analogues. With the more bulky sulfur atom, the relatively small τ_1 angle for the title molecule as well as for (2) and (3) is still somewhat surprising since it gives rise to a short non-bonding intramolecular C3...S1 distance of 3.046 (4) Å [*cf.* the sum of van der Waals radii 3.5 Å; related distances are 3.061 in (2) and 3.104 Å in (3)]. This distance could be increased by twisting the phenyl ring further out of the plane of atoms C4, C7 and S1, as in the case of (1) with a corresponding C...S distance of 3.23 Å.

In order to explain this conformational feature of the title compound, molecular-mechanics calculations using the program *MMPMI* (Gilbert & Gajewski, 1985) were carried out. By optimization of the molecular geometry starting from the X-ray structure the minimum energy has been found for a conformation including a τ_1 value of -60 $^\circ$. Varying τ_1 in 10 $^\circ$ steps from -80 to +140 $^\circ$ and optimizing the remaining geometrical parameters at each τ_1 value, the calculation gave the highest energy for $\tau_1 = 30^\circ$ with the difference from the minimum energy of about 16 kJ mol $^{-1}$. The τ_1 value of -14.6 $^\circ$ found experimentally within the crystal structure corresponds to an energy 8 kJ mol $^{-1}$ above the minimum value, which may be easily explained by packing forces. The τ_1 values in (1), (2) and (3) are closer to the minimum-energy conformation for the isolated molecule and correspond to energy differences of ~0, 2 and 4 kJ mol $^{-1}$, respectively.

The phenyl ring has usual geometrical parameters, the mean bond length and angle being 1.384 (8) Å and 120.0 (1.7) $^\circ$.

Fig. 2 shows the molecular packing in a projection along *a*. From the intermolecular atom-atom distances, no special contacts besides van der Waals interactions are recognizable.

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References

- BORGULYA, J., DALY, J. J., SCHONHOLZER, P. & BERNAUER, K. (1984). *Helv. Chim. Acta*, **67**, 1827-1842.
 BULMAN-PAGE, P. C., CHADWICK, D. J., VAN NIEL, M. B. & WESTWOOD, D. (1987). *Acta Cryst.* **C43**, 803-804.
 BURKERT, U. & ALLINGER, N. L. (1982). *Molecular Mechanics*, ACS Monograph No. 177. Washington, DC: American Chemical Society.
 GILBERT, K. E. & GAJEWSKI, J. J. (1985). *MMPMI*. Version 1.000. Indiana Univ., USA.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KALFF, H. T. & ROMERS, C. (1966). *Acta Cryst.* **20**, 490-496.

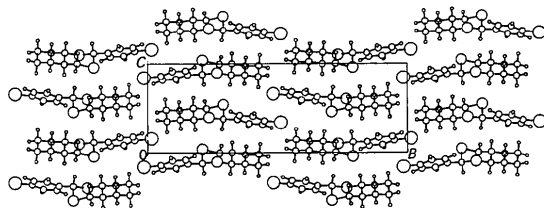


Fig. 2. Molecular packing arrangement projected along [100] in a *PLUTO* drawing (Motherwell & Clegg, 1978).

- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- RIZZOLI, C., SANGERMANO, V., CALESTANI, G. & ANDRETTI, G. D. (1987). *J. Appl. Cryst.* **20**, 436–439.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRIK, G. M. (1986). *SHELXS86*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
- Syntax (1973). *XTL Structure Determination System*. Syntax Analytical Instruments, Cupertino, California, USA.
- TSCHERSKE, C., JOACHIMI, D., VORBRODT, H.-M., ZASCHKE, H., WIEGELEBEN, A., HAUSER, A. & DEMUS, D. (1989). *Liq. Cryst.* **5**, 177–190.
- TSCHERSKE, C., KLEINPETER, E., KÖHLER, H. & ZASCHKE, H. (1990). In preparation.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 159–166.
- ZEFIROV, N. S. & KASIMIRCHIK, V. (1974). *Usp. Khim.* **43**, 252–265.

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Structure of *exo,endo,endo*-9,9,10,11,12-Pentabromotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene

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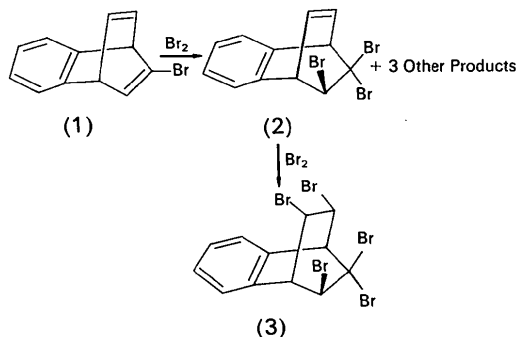
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Abstract. C₁₂H₉Br₅, *M*_r = 552.723, triclinic, *P* $\bar{1}$, *a* = 10.441 (1), *b* = 12.406 (1), *c* = 6.887 (1) Å, α = 90.82 (1), β = 124.01 (1), γ = 102.73 (1)°, *V* = 710.8 Å³, *Z* = 2, *D*_m = 2.56, *D*_x = 2.582 g cm⁻³, $\lambda(\text{Cu } K\alpha)$ = 1.54180 Å, μ = 171.38 cm⁻¹, *F*(000) = 512, *T* = 293 K, *R* = 0.034 for 2045 observed reflections. X-ray analysis of the title compound shows that the skeleton of the molecule is not changed after two successive bromination reactions. The addition of the second Br₂ molecule occurs contrary to our expectation in a *syn* fashion. This is probably due to interactions with neighbouring Br atoms.

Introduction. Benzobarrelene (1,4-dihydro-1,4-ethenonaphthalene) is an ideal compound for di- π -methane rearrangement (Hixon, Mariano & Zimmerman, 1973). In particular, the introduction of a substituent in a vinyl location increases the number of possible initial bonding modes. Therefore, one may obtain more insight into the mechanism of the di- π -methane rearrangement and the effect of substituents. Recently, an efficient synthetic route leading to monosubstituted benzobarrelene derivatives has been developed (Balci, Çakmak & Harmandar, 1985). As an extension of this work, an alternative large-scale preparation of disubstituted benzobarrelene derivatives has been undertaken (Çakmak & Balci, 1989). We were also interested in the synthesis of trisubstituted benzobarrelenes (Çakmak, Hökelek & Balci, 1990).

For this purpose we carried out the bromination of (1) refluxing in CCl₄ and isolated four bromination products. One of these, isomer (2), was subjected to further bromination and only one isomer was obtained. In order to gain more knowledge of the reaction mechanism and the structure of the product, we carried out an X-ray structure analysis of isomer (3).



Experimental. The compound was dissolved in boiling chloroform and *n*-hexane added. The clear solution was cooled slowly at room temperature. In about 6 h, the colourless rod-shaped crystals (m.p. 453 K) were obtained.

Initially, the cell had the parameters *a* = 6.887, *b* = 8.718, *c* = 12.406 Å and α = 74.03, β = 89.18, γ = 83.10° with the matrix elements 00 $\bar{1}$, $\bar{1}0\bar{1}$, 010. But we re-refined the standard cell with the matrix

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