Fig. 3. Vue stéréoscopique de la molécule.

conduit à la valeur finale $R = 0,054$.* Le Tableau 1 donne les coordonnées fractionnaires et les coefficients d'agitation thermique de la molécule. Les Figs. 1 et 2 résument les distances interatomiques et angles valentiels principaux.

Discussion. La géométrie moléculaire du composé étudié ici est illustrée à l'aide d'une vue stéréoscopique (Johnson, 1965) sur la Fig. 3: la jonction entre les cycles à cinq et sept carbones est *cis*, les cycles aromatiques sont rigoureusement plans, le cycle à cinq chaînons se trouve dans le même plan que le noyau

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* La liste des facteurs de structure, les coefficients des tenseurs d'agitation thermique anisotrope, les paramètres des atomes d'hydrogène, les plans moyens et les angles dièdres entre ces plans sont déposés au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 36115: 19 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.

benzénique accolé, et le cycle saturé à sept carbones présente une conformation chaise. Toutes les distances intermoléculaires sont supérieures aux sommes des rayons de van der Waals des atomes.

Par ailleurs la géométrie *cis* des indanones pour lesquelles $n = 3$ avait été envisagée de façon quasi certaine par résonance magnétique nucléaire (Essiz, 1979) et avec $n = 4$ une forte présomption existait. Le fait que pour $n = 5$, la jonction *cis* soit établie sans ambiguïté par ce travail, conforte les résultats précédents. En effet il est très improbable que les condensations aryniques qui permettent les synthèses de ces produits conduisent à une jonction différente pour $n < 5$ alors que la tension des cycles est plus forte que pour $n = 5$.

Références

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
ESSIZ, M. (1979). Thèse de Doctorat ès Sciences. Univ. de Nancy.
ESSIZ, M., GUILLAUMET, G. & CAUBÈRE, P. (1979). *Tetrahedron*, **35**, 1167–1171.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. de York, Angleterre, et Louvain, Belgique.

The Twin-Chair Conformation of Bicyclo[3.3.1]nonane: X-ray Diffraction Study of 2,6-Dichloro-9λ⁶-thiabicyclo[3.3.1]nonane 9,9-Dioxide

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Abstract. $C_8H_{12}Cl_2O_2S$, monoclinic, $C2/c$, $a = 11.543$ (4), $b = 9.342$ (5), $c = 19.754$ (4) Å, $\beta = 103.36$ (3)°, $U = 2073$ Å³, $Z = 8$, $D_c = 1.56$ Mg m⁻³, $F(000) = 1008$, μ(Mo $K\alpha$) = 7.1 mm⁻¹, $R = 0.045$ for 1863 reflections. The molecule has a twin-chair conformation with a $C(3) \cdots C(7)$ transannular separation of 3.120 (4) Å. The chloro substituents at positions 2 and 6 cause a notable skewing of the rings.

Introduction. X-ray diffraction studies of bicyclo[3.3.1]nonane derivatives have shown that the twin-chair conformer is characterized by a $C(3) \cdots C(7)$ separation of *ca* 3.1 Å and that the H···H 3,7 separation is shorter than 2 Å, though the actual value is not yet known with precision (Bovill, Cox, Flitman, Guy, Hardy, McCabe, Macdonald, Sim & White, 1979; Sim, 1979). Calculations of the H···H 3,7

separation by the method of molecular mechanics have produced estimates that range from 1·97 to 2·20 Å (*e.g.* White & Bovill, 1976, 1977; Peters, Baas, van de Graaf, van der Toorn & van Bekkum, 1978; Allinger, Tribble, Miller & Wertz, 1971); accordingly, the geometry of the twin-chair conformer provides a test of the relative merits of the empirical force fields employed in conformational calculations. The investigation of the title compound was undertaken to determine the conformational effect of substituents at positions 2 and 6.

A small crystal was used for intensity measurements on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation, and 1863 independent reflections in the range $\theta < 28°$ satisfied the criterion $I > 2 \cdot 5\sigma(I)$. The structure was solved with a version of *MULTAN* (Germain, Main & Woolfson, 1971) modified by Dr C. J. Gilmore. Subsequent calculations were performed with *SHELX* (Sheldrick, 1976). Coordinates and anisotropic thermal parameters of the S, Cl, C and O atoms were adjusted by full-matrix least-squares calculations with unit weights ($R = 0.069$) after which the H atoms were located in a difference map. The positional and isotropic thermal parameters of the H atoms were then included as variables and the weighting scheme was altered to $w \propto 1/\sigma^2(F)$. The calculations converged at $R = 0.045$, $R_w = 0.048$.*

Discussion. The molecular structure is shown in Fig. 1. The atomic coordinates are listed in Table 1, bond

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36120 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
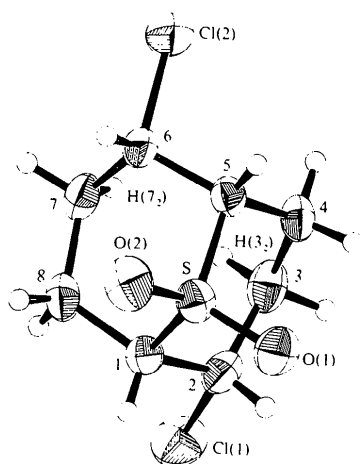
lengths and angles in Table 2, and torsion angles in Table 3.

The six-membered rings are skewed, the torsion angles S—C(1)—C(2)—C(3) and S—C(5)—C(4)—C(3) differing by 7·6°, as do the torsion angles S—C(1)—

Table 1. *Atomic coordinates* ($\times 10^4$ *for* Cl, S, O *and* C; $\times 10^3$ *for* H) *and isotropic thermal parameters* ($Å^2 \times 10^3$)

For nonhydrogen atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}/U
Cl(1)	8474 (1)	2438 (1)	2254 (1)	59 (1)
Cl(2)	2952 (1)	2969 (1)	1235 (1)	68 (1)
S	5915 (1)	2306 (1)	296 (1)	36 (1)
O(1)	6404 (2)	997 (2)	94 (1)	52 (1)
O(2)	5543 (2)	3375 (2)	−232 (1)	52 (1)
C(1)	6926 (2)	3060 (3)	1029 (1)	35 (1)
C(2)	7289 (2)	1832 (3)	1549 (1)	40 (1)
C(3)	6292 (3)	1196 (3)	1844 (1)	45 (1)
C(4)	5184 (3)	790 (3)	1281 (1)	40 (1)
C(5)	4733 (2)	1899 (3)	707 (1)	34 (1)
C(6)	4262 (2)	3331 (3)	911 (1)	39 (1)
C(7)	5144 (3)	4193 (3)	1445 (2)	43 (1)
C(8)	6352 (3)	4391 (3)	1265 (1)	39 (1)
H(1)	758 (3)	328 (3)	87 (2)	44 (8)
H(2)	760 (3)	112 (4)	132 (2)	51 (9)
H(3$_1$)	664 (3)	26 (4)	211 (2)	63 (9)
H(3$_2$)	609 (3)	195 (4)	216 (2)	52 (8)
H(4$_1$)	454 (3)	56 (3)	150 (2)	42 (7)
H(4$_2$)	536 (3)	−10 (4)	103 (2)	46 (8)
H(5)	417 (3)	149 (3)	35 (2)	43 (8)
H(6)	399 (3)	386 (4)	51 (2)	60 (9)
H(7$_1$)	477 (3)	507 (3)	147 (2)	62 (9)
H(7$_2$)	519 (3)	372 (3)	191 (2)	36 (7)
H(8$_1$)	627 (3)	508 (3)	90 (2)	51 (8)
H(8$_2$)	691 (3)	475 (3)	171 (2)	57 (9)

Fig. 1. *ORTEP* diagram (Johnson, 1965) of the molecule. The thermal ellipsoids of the Cl, S, O and C atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0·1 Å.

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

S—O(1)	1·442 (2)	C(8)—C(1)	1·532 (4)
S—O(2)	1·436 (2)	C(1)—H(1)	0·91 (3)
S—C(1)	1·782 (2)	C(2)—H(2)	0·92 (3)
S—C(5)	1·782 (3)	C(3)—H(3$_1$)	1·05 (3)
Cl(1)—C(2)	1·803 (3)	C(3)—H(3$_2$)	1·00 (3)
Cl(2)—C(6)	1·806 (3)	C(4)—H(4$_1$)	0·97 (3)
C(1)—C(2)	1·533 (4)	C(4)—H(4$_2$)	1·01 (3)
C(2)—C(3)	1·525 (4)	C(5)—H(5)	0·93 (3)
C(3)—C(4)	1·535 (4)	C(6)—H(6)	0·93 (3)
C(4)—C(5)	1·536 (3)	C(7)—H(7$_1$)	0·93 (3)
C(5)—C(6)	1·532 (4)	C(7)—H(7$_2$)	1·00 (3)
C(6)—C(7)	1·517 (4)	C(8)—H(8$_1$)	0·95 (3)
C(7)—C(8)	1·528 (5)	C(8)—H(8$_2$)	1·01 (3)
O(1)—S—O(2)	117·3 (1)	Cl(1)—C(2)—C(1)	108·9 (2)
O(1)—S—C(1)	109·6 (1)	C(2)—C(3)—C(4)	113·3 (2)
O(1)—S—C(5)	109·5 (1)	C(3)—C(4)—C(5)	116·8 (2)
O(2)—S—C(1)	110·2 (1)	C(4)—C(5)—S	108·4 (2)
O(2)—S—C(5)	110·3 (1)	C(4)—C(5)—C(6)	118·3 (2)
C(1)—S—C(5)	98·1 (1)	C(6)—C(5)—S	106·8 (2)
S—C(1)—C(2)	105·9 (2)	C(5)—C(6)—C(7)	115·1 (2)
S—C(1)—C(8)	108·7 (2)	C(5)—C(6)—Cl(2)	107·9 (2)
C(2)—C(1)—C(8)	118·3 (2)	C(7)—C(6)—Cl(2)	109·6 (2)
C(1)—C(2)—C(3)	115·8 (2)	C(6)—C(7)—C(8)	113·9 (2)
Cl(1)—C(2)—C(3)	109·4 (2)	C(7)—C(8)—C(1)	117·0 (2)

Table 3. *Torsion angles* (°)

S C(1) C(2) C(3)	−64·4 (3)	S C(5)−C(6)−C(7)	−64·0 (3)
C(1) C(2) -C(3)−C(4)	50·6 (3)	C(5)−C(6) -C(7)-C(8)	50·6 (3)
C(2) -C(3)−C(4)−C(5)	−46·2 (3)	C(6)−C(7)−C(8)-C(1)	−46·7 (3)
C(3) -C(4)-C(5)−S	56·8 (3)	C(7)−C(8)−C(1)−S	56·4 (3)
C(3) C(4) C(5) C(6)	64·9 (3)	C(7)- C(8)−C(1)−C(2)	−64·3 (3)
C(4) C(5) S C(1)	63·1 (2)	C(8)−C(1)−S−C(5)	−61·9 (2)
C(4)−C(5)−S−O(1)	51·2 (2)	C(8)−C(1)−S−O(2)	53·3 (2)
C(4) C(5) S O(2)	−178·2 (2)	C(8)−C(1)−S−O(1)	−176·1 (2)
C(5) S−C(1)−C(2)	66·2 (2)	C(1)−S−C(5)−C(6)	65·5 (2)
O(1) S C(1) C(2)	48·0 (2)	O(2) S−C(5)−C(6)	−49·7 (2)
O(2) S C(1) C(2)	−178·6 (2)	O(1)−S−C(5)−C(6)	179·7 (2)
Cl(1) C(2)- C(1)- S	171·9 (1)	Cl(2)- C(6)−C(5)−S	173·3 (1)
Cl(1) C(2) C(1) C(8)	66·0 (3)	Cl(2)--C(6)−C(5)−C(4)	−64·1 (3)
Cl(1) C(2) C(3) C(4)	174·0 (2)	Cl(2) -C(6)−C(7)−C(8)	172·4 (2)
C(8)- C(1)−C(2)−C(3)	57·7 (3)	C(4)−C(5)−C(6)−C(7)	58·6 (3)

C(8)−C(7) and S−C(5)−C(6)−C(7). Accordingly, the symmetry of the carbon framework is lowered from C_{2v} and approximates closely to C_2. Within the rings, the C−C−C angles at C(2) and C(6) are 115·8 (2) and 115·1 (2)° whereas those at C(4) and C(8) are slightly larger, 116·8 (2) and 117·0 (2)°. The angles at C(3) and C(7) are rather smaller, 113·3 (2) and 113·9 (2)°, and the S−C−C angles at C(1) and C(5) are substantially smaller, 105·9−108·7, mean 107·5°.

The C(3)···C(7) and H(3₂)···H(7₂) separations obtained from the final coordinates are 3·120 (4) and 1·96 (4) Å. However, the C(3)−H(3₂) and C(7)−H(7₂) lengths of 1·00 Å are shorter than the normal spectroscopic value for C(sp^3)−H bonds, a recognized artifact of the X-ray diffraction method, and when H(3₂) and H(7₂) are displaced along the C−H vectors to make these C−H distances 1·10 Å the H···H transannular distance becomes 1·85 Å. Some molecular-mechanics calculations estimate the H···H 3,7 separation in bicyclo|3.3.1|nonane to be greater than 2 Å and

clearly exaggerate the transannular repulsion. The C(3)···C(7) separation reported here differs slightly from the value of 3·10 Å obtained for bicyclo|3.3.1|-nonane in an electron diffraction study (Osina, Mastryukov, Vilkov & Belikova, 1976).

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References

ALLINGER, N. L., TRIBBLE, M. T., MILLER, M. A. & WERTZ, D. H. (1971). *J. Am. Chem. Soc.* **93**, 1637–1648.

BOVILL, M. J., COX, P. J., FLITMAN, H. P., GUY, M. H. P., HARDY, A. D. U., McCABE, P. H., MACDONALD, M. A., SIM, G. A. & WHITE, D. N. J. (1979). *Acta Cryst.* B**35**, 669–675.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

OSINA, E. L., MASTRYUKOV, V. S., VILKOV, L. V. & BELIKOVA, N. A. (1976). *J. Chem. Soc. Chem. Commun.* pp. 12–13.

PETERS, J. A., BAAS, J. M. A., VAN DE GRAAF, B., VAN DER TOORN, J. M. & VAN BEKKUM, H. (1978). *Tetrahedron*, **34**, 3313–3323.

SHELDRICK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.

SIM, G. A. (1979). *Acta Cryst.* B**35**, 2455–2458.

WHITE, D. N. J. & BOVILL, M. J. (1976). *J. Mol. Struct.* **33**, 273–277.

WHITE, D. N. J. & BOVILL, M. J. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1610–1623.

Structure of (+)-*cis*-9-(3-Dimethylaminopropyl)-10-methyl-2-(trifluoromethyl)-9,10-dihydroanthracene Methyliodide Benzene Solvate at 168 K

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Abstract. $C_{21}H_{24}F_3N.CH_3I.C_6H_6$, orthorhombic, $P2_12_12_1$, $Z = 4$, $M_r = 567·49$, $a = 8·026$ (2), $b = 11·623$ (2), $c = 29·389$ (4) Å, $V = 2741·6$ (8) Å^3, $T = 168$ K, $D_x = 1·375$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 9·40 mm^{-1}, final $R = 0·047$ for 1621 observed reflections. Both the *meso* substituents are in the 'boat–axial' conformation with respect to the central ring of the dihydroanthracene ring system. The

absolute configuration of the title molecule was determined by using the anomalous-scattering effect and is the same as that determined from room-temperature data.

Introduction. Single crystals of the methyliodide of *cis*-9-(3-dimethylaminopropyl)-10-methyl-2-(trifluoro-methyl)-9,10-dihydroanthracene (I) (assigned as