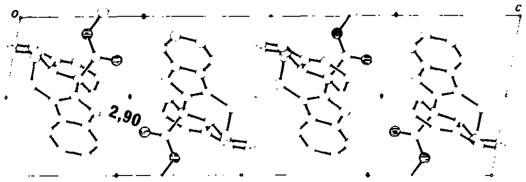

Fig. 4. Projection xOz. Les atomes d'azote sont représentés par des cercles pointillés, les atomes d'oxygène par des cercles hachurés.

Comme cela a déjà été observé (Riche, 1974; Falkenberg & Carlström, 1971) le noyau indolique est légèrement plié le long de la liaison C(13)—C(9). Le benzène et le pyrrole sont plans et les normales à ces deux plans font entre elles un angle de 1,8°. Le cycle à sept chaînons *C* est dans une conformation demi-chaise. Le cycle *E* adopte la conformation demi-chaise idéale du cyclohexène (Bucourt & Hainaut, 1965) alors que le cycle *D* adopte une conformation sofa. Le système des doubles liaisons conjuguées 14–15 et 19–20, n'est plan qu'en première approximation, l'angle entre les deux normales aux plans moyens des doubles liaisons 14–15 (plan *D*, Tableau 5) et 20–19 (plan *E*, Tableau 5) étant de 8,5°. Par ailleurs, les quatre atomes C(16), C(2), C(7) et C(6) ne sont pas coplanaires.

Le groupement méthoxycarbonyl est pratiquement plan, le méthyle C(25) étant à 0,06 Å du plan moyen des quatre autres atomes. Notons que l'atome d'oxygène O(24) éclipse parfaitement l'atome C(21) [angle de torsion C(21)—C(16)—C(22)—O(24) = 1°]. Cette conformation, *a priori* peu favorable, est probablement stabilisée par le système de liaisons hydrogène. Dans le cristal, en effet, les molécules forment des dimères autour d'un axe binaire (Fig. 4). Deux molécules sont liées entre elles par deux liaisons hydrogène du type N(1)—H···O(24) dont les caractéristiques géométriques sont: N···O = 2,90, N—H = 0,89, H···N = 2,06 Å et N—H···O = 158°.

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A Skewed Bicyclo[3.3.1]nonane. X-ray and Neutron Diffraction Studies of 9-Thiabicyclo[3.3.1]nonane-2,6-dione and Molecular-Mechanics Calculations for Bicyclo[3.3.1]nonane Derivatives

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Abstract

The crystal structure of 9-thiabicyclo[3.3.1]nonane-2,6-dione has been determined from X-ray and neutron diffraction measurements. The crystals are orthorhombic, with a = 10·731 (4), b = 6·806 (1), c = 10·771 (2) Å, Z = 4, space group $Pbcn$. The molecule has C_2 symmetry in the crystal. Full-matrix least-squares refinement converged at R = 0·053 for 556 X-ray and R = 0·093 for 455 neutron reflections. The molecule has a twin-chair conformation with the rings appreciably distorted from ideal cyclohexane geometry,

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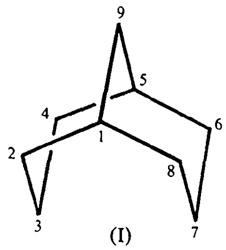
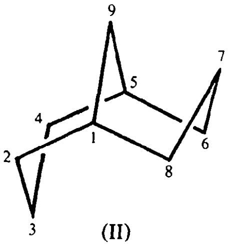
both by skewing and by direct outward displacement of the C(3) and C(7) methylene groups; the transannular H···H separation at these methylene groups is 2·07 (2) Å. Molecular-mechanics calculations are reported for this and other bicyclo[3.3.1]nonanes.



(I)



(II)

Derivatives of bicyclo[3.3.1]nonane can exist as twin-chair (I) or boat–chair (II) conformers. A hypothetical twin-chair conformer constructed from ideal cyclohexane rings with tetrahedral valency angles would have a prohibitively short transannular separation of 0·75 Å between H atoms on the 3 and 7 methylene groups; the alternative boat–chair conformer, on the other hand, avoids the strain of the 3···7 interaction but has the unfavourable torsional and steric features associated with the boat conformation of cyclohexane. Various X-ray studies have established that molecules lacking *endo* substituents at position 3 or 7 generally adopt a modified twin-chair conformation in which the rings are appreciably flattened so as to increase the transannular H···H separation (Brown, Eglinton, Martin, Parker & Sim, 1964; Dobler & Dunitz, 1964; Brown, Martin & Sim, 1965; Webb & Becker, 1967; Smith, 1972; Brauer & Krüger, 1973) and equilibration measurements indicate that this twin-chair conformation is more stable than the boat–chair conformation by *ca* 13 kJ mol^{-1} (Appleton, Egan, Evans, Graham & Dixon, 1968; Marvell & Knutson, 1970). Other X-ray studies have confirmed that molecules with bulky *endo* substituents at positions 3 or 7 prefer the boat–chair conformation (Tamura & Sim, 1968; Cradwick & Sim, 1971). 1-Methyl-7-*exo*-*tert*-butylbicyclo[3.3.1]nonane-2,9-dione adopts the boat–chair conformation though it has an *exo* rather than an *endo* substituent at position 7 and it has been suggested that this result can be attributed to the buttressing effect of the bulky *tert*-butyl group and to the relatively small enthalpy difference between chair and boat conformations of 1,3-cyclohexanedione (Hickmott, Cox & Sim, 1974). 9-Oxa-3,7-dithiabicyclo[3.3.1]nonane has also been found to adopt the boat–chair conformation, though it lacks an *endo* substituent, and this has been ascribed to lone-pair repulsions between the S atoms (Zefirov, Rogozina, Kurkutova, Goncharov & Belov, 1974).

Investigations of bicyclo[3.3.1]nonane by electron diffraction (Osina, Mastryukov, Vilkov & Belikova, 1976) and bicyclo[3.3.1]nonan-9-one by microwave spectroscopy (Laird & Tyler, 1977) have confirmed that these molecules adopt flattened twin-chair conformations in the gas phase.

There has been considerable discussion of the most appropriate choice of H··· H potential-energy function for molecular-mechanics calculations of conformations and steric energies (Hendrickson, 1967; Allinger & Sprague, 1972; Engler, Andose & Schleyer, 1973; Ermer & Lifson, 1973; Fitzwater & Bartell, 1976; Allinger, 1976; White & Bovill, 1976, 1977). Intramolecular H···H repulsive interactions are important features of various organic compounds, *e.g.* cyclodecane (Dunitz, 1968), and H···H distances in strained molecules can serve to calibrate the force field employed in these conformational calculations. X-ray structure determinations have yielded accurate values for the C(3)···C(7) separations in twin-chair bicyclo[3.3.1]nonanes but have inevitably given rather imprecise estimates of the critical H···H distances. To define these adequately it is necessary to resort to neutron diffraction.

Among various bicyclo[3.3.1]nonane derivatives available to us, 9-thiabicyclo[3.3.1]nonane-2,6-dione could be obtained in the form of reasonably large single crystals and we have subjected this compound to both X-ray and neutron diffraction investigations.

Crystal data

9-Thiabicyclo[3.3.1]nonane-2,6-dione, $C_8H_{10}O_2S$, $M_r = 170{\cdot}2$. Orthorhombic, $a = 10{\cdot}731$ (4), $b = 6{\cdot}806$ (1), $c = 10{\cdot}771$ (2) Å, $U = 786{\cdot}7$ Å^3, $D_c = 1{\cdot}44$, $Z = 4$, space group *Pbcn*, molecular symmetry in crystal C_2. The cell dimensions were derived from X-ray measurements on a four-circle diffractometer with Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å. For the neutron analysis, a crystal of volume 21·0 mm^3 was obtained from chloroform/petrol solution.

X-ray measurements

The intensities of 556 independent reflections with $I > 3\sigma(I)$ were measured on a Hilger & Watts computer-controlled four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. The 2θ–ω step-scan procedure was employed and the θ limit was 28°. Absorption was neglected ($\mu = 0{\cdot}348$ mm^{-1}).

Neutron measurements

For the neutron intensity measurements we used a Grubb–Parsons four-circle diffractometer at AERE, Harwell. The neutron wavelength was 1·180 Å. Reflections were surveyed in the range $\theta \leq 55°$ by the

2θ–ω step-scan procedure and 455 independent intensity measurements with $I > 3\sigma(I)$ obtained. The intensities were corrected for absorption (Gaussian numerical integration, $\mu = 0{\cdot}179$ mm^{-1}) by the program *ABSORB* in the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Structure analysis

The crystal structure was elucidated from the X-ray intensities by direct phase determination. After preliminary least-squares adjustment of the parameters of the C, O and S atoms, the H atoms were located from a difference map. Subsequent full-matrix least-squares calculations, with isotropic thermal parameters for the H atoms and anisotropic parameters for the others, converged at $R = 5{\cdot}3\%$. Scattering factors for C, O and S were taken from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Dispersion corrections for S were taken from *International Tables for X-ray Crystallography* (1962). Unit weights were used.

The final parameters from the X-ray analysis were used as the starting point for the least-squares analysis of the neutron data. The nuclear scattering lengths were: S 0·280, O 0·580, C 0·665, H –0·374 × 10^{-11} mm (Bacon, 1972). The positional and anisotropic thermal parameters of all atoms were adjusted by full-matrix calculations and refinement converged at $R = 9{\cdot}3\%$ (unit weights).*

Results and discussion

The positional parameters of the atoms are listed in Table 1; the neutron results are given first, followed by the X-ray results. The bond lengths, valency angles,

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

The neutron results are given first and are followed by the X-ray results.

	x	*y*	*z*
C(1)	0·5575 (4)	0·8108 (6)	0·3614 (4)
	0·5564 (4)	0·8099 (6)	0·3614 (4)
C(2)	0·4427 (4)	0·7056 (6)	0·4112 (4)
	0·4427 (4)	0·7054 (6)	0·4104 (4)
C(3)	0·3692 (4)	0·5814 (7)	0·3196 (5)
	0·3702 (5)	0·5814 (7)	0·3199 (4)
C(4)	0·3413 (4)	0·6797 (7)	0·1948 (4)
	0·3420 (5)	0·6790 (7)	0·1940 (4)
O(2)	0·4123 (7)	0·7209 (10)	0·5172 (6)
	0·4120 (3)	0·7197 (5)	0·5172 (3)
S(9)	0·5000	0·9937 (2)	0·2500
	0·5000	0·9917 (2)	0·2500
H(1)	0·5960 (11)	0·8963 (18)	0·4393 (10)
	0·5900 (43)	0·8822 (59)	0·4318 (41)
H(3_1)	0·4217 (11)	0·4469 (15)	0·3062 (13)
	0·4237 (48)	0·4589 (74)	0·3217 (43)
H(3_2)	0·2816 (11)	0·5417 (18)	0·3635 (12)
	0·2805 (57)	0·5440 (89)	0·3660 (62)
H(4_1)	0·2585 (8)	0·7680 (19)	0·2039 (11)
	0·2786 (41)	0·7625 (68)	0·2048 (35)
H(4_2)	0·3162 (11)	0·5647 (15)	0·1248 (12)
	0·3280 (39)	0·5821 (57)	0·1340 (38)

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

The neutron results are given first and are followed by the X-ray results.

C(1)—C(2)	1·522 (6)	C(1)—H(1)	1·102 (12)
	1·507 (6)		0·97 (4)
C(1)—S(9)	1·835 (4)	C(3)—H(3_1)	1·085 (11)
	1·827 (4)		1·01 (5)
C(2)—C(3)	1·521 (6)	C(3)—H(3_2)	1·086 (12)
	1·506 (6)		1·11 (6)
C(2)—O(2)	1·191 (7)	C(4)—H(4_1)	1·077 (11)
	1·200 (5)		0·89 (5)
C(3)—C(4)	1·530 (6)	C(4)—H(4_2)	1·120 (12)
	1·540 (6)		0·94 (4)
C(4)—C(5)	1·531 (6)		
	1·529 (6)		

Table 3. *Valency angles* (°)

S(9)—C(1)—C(2)	106·1 (3)	H(3_1)—C(3)—C(2)	106·6 (7)
O(2)—C(2)—C(1)	121·2 (4)	H(3_2)—C(3)—C(2)	107·7 (7)
C(3)—C(2)—C(1)	116·9 (3)	H(3_1)—C(3)—C(4)	110·8 (8)
O(2)—C(2)—C(3)	121·9 (4)	H(3_2)—C(3)—C(4)	108·8 (7)
C(4)—C(3)—C(2)	115·4 (3)	H(3_2)—C(3)—H(3_1)	107·3 (9)
C(5)—C(4)—C(3)	117·6 (3)	H(4_2)—C(4)—C(3)	109·4 (7)
C(6)—C(5)—C(4)	116·1 (3)	H(4_1)—C(4)—C(5)	107·2 (7)
S(9)—C(5)—C(4)	112·0 (3)	H(4_2)—C(4)—C(5)	108·2 (6)
C(5)—S(9)—C(1)	94·6 (6)	H(4_1)—C(4)—C(3)	109·0 (7)
H(1)—C(1)—C(2)	106·4 (6)	H(4_2)—C(4)—H(4_1)	104·6 (9)
H(1)—C(1)—S(9)	105·4 (7)	H(5)—C(5)—C(4)	110·1 (7)

Table 4. *Torsion angles* (°)

C(8)—C(1)—C(2)—C(3)	−59·1 (5)	O(2)—C(2)—C(3)—H(3_1)	−103·7 (8)
C(8)—C(1)—C(2)—O(2)	121·1 (5)	O(2)—C(2)—C(3)—H(3_2)	11·2 (9)
S(9)—C(1)—C(2)—C(3)	66·1 (4)	C(2)—C(3)—C(4)—H(4_1)	−84·6 (7)
S(9)—C(1)—C(2)—O(2)	−113·7 (5)	C(2)—C(3)—C(4)—H(4_2)	161·5 (7)
C(2)—C(1)—S(9)—C(5)	−66·5 (3)	H(3_1)—C(3)—C(4)—C(5)	−83·5 (8)
C(8)—C(1)—S(9)—C(5)	61·2 (3)	H(3_1)—C(3)—C(4)—H(4_1)	154·2 (9)
C(1)—C(2)—C(3)—C(4)	−46·9 (5)	H(3_1)—C(3)—C(4)—H(4_2)	40·3 (10)
O(2)—C(2)—C(3)—C(4)	132·9 (5)	H(3_2)—C(3)—C(4)—C(5)	158·8 (7)
C(2)—C(3)—C(4)—C(5)	37·6 (5)	H(3_2)—C(3)—C(4)—H(4_1)	36·5 (10)
C(3)—C(4)—C(5)—C(6)	71·1 (5)	H(3_2)—C(3)—C(4)—H(4_2)	−77·3 (10)
C(3)—C(4)—C(5)—S(9)	−51·0 (4)	C(3)—C(4)—C(5)—H(5)	168·0 (7)
S(9)—C(5)—C(6)—O(6)	−113·7 (5)	H(4_1)—C(4)—C(5)—C(6)	−165·7 (7)
C(4)—C(5)—S(9)—C(1)	61·2 (3)	H(4_1)—C(4)—C(5)—S(9)	72·2 (7)
C(6)—C(5)—S(9)—C(1)	66·5 (3)	H(4_1)—C(4)—C(5)—H(5)	−44·8 (10)
H(1)—C(1)—C(2)—C(3)	178·0 (7)	H(4_2)—C(4)—C(5)—C(6)	−53·4 (7)
H(1)—C(1)—C(2)—O(2)	−1·8 (9)	H(4_2)—C(4)—C(5)—S(9)	175·5 (6)
H(1)—C(1)—S(9)—C(5)	179·1 (7)	H(4_2)—C(4)—C(5)—H(5)	67·5 (10)
C(1)—C(2)—C(3)—H(3_1)	76·5 (8)	H(5)—C(5)—C(6)—C(7)	178·0 (7)
C(1)—C(2)—C(3)—H(3_2)	−168·6 (7)	H(5)—C(5)—S(9)—C(1)	−179·1 (7)

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* Structure factors, thermal parameters, and force constants have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34069 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

torsion angles and intermolecular separations are given in Tables 2–5. The agreement between the structural results of the two analyses is excellent and, accordingly, in Table 2 both sets of interatomic distances are provided for comparison but in the other tables only the neutron results are given. Fig. 1 shows a general view of the molecule, while Fig. 2 illustrates the packing. The molecule has crystallographic C_2 symmetry and the coordinates of C(5), C(6), *etc.* are derived from those of C(1), C(2), *etc.* by the transformation $1-x, y, \frac{1}{2}-z$.

The $C(sp^3)$–$C(sp^3)$ lengths, mean 1·533 Å (averaged over neutron and X-ray results) are, as expected, slightly longer than the $C(sp^3)$–$C(sp^2)$ values, mean 1·514 Å. The C–H distances are 1·077–1·120, mean 1·094 Å (neutron), and 0·89–1·11, mean 0·98 Å (X-ray); here the neutron analysis gives the expected improvement in accuracy. For comparison, the C–H distances obtained in a neutron diffraction study of 1,6-cyclodecanediol are 1·053–1·120, mean 1·092 Å (Ermer, Dunitz & Bernal, 1973).

Table 5. *Intermolecular separations* <3 Å

$H(4_1)\cdots H(4_2^{I})$	2·33	$H(4_1)\cdots O(2^{V})$	2·72
$H(4_2)\cdots O(2^{II})$	2·49	$H(1)\cdots H(1^{III})$	2·82
$H(4_1)\cdots H(3_1^{II})$	2·54	$H(4_1)\cdots C(3^{I})$	2·83
$H(4_1)\cdots H(3_2^{I})$	2·57	$H(3_1)\cdots O(2^{VI})$	2·85
$H(1)\cdots O(2^{III})$	2·65	$H(4_2)\cdots H(3_2^{II})$	2·93
$H(1)\cdots H(4_2^{IV})$	2·72	$H(1)\cdots H(3_2^{VII})$	2·94

The superscripts refer to the following transformations of the atomic coordinates:

(I)	$\frac{1}{2}-x,$	$\frac{1}{2}+y,$	z	(V)	$\frac{1}{2}-x,$	$1\frac{1}{2}-y,$	$-\frac{1}{2}+z$
(II)	$x,$	$1-y,$	$-\frac{1}{2}+z$	(VI)	$1-x,$	$1-y,$	$1-z$
(III)	$1-x,$	$2-y,$	$1-z$	(VII)	$\frac{1}{2}+x,$	$1\frac{1}{2}-y,$	$1-z.$
(IV)	$\frac{1}{2}+x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$				

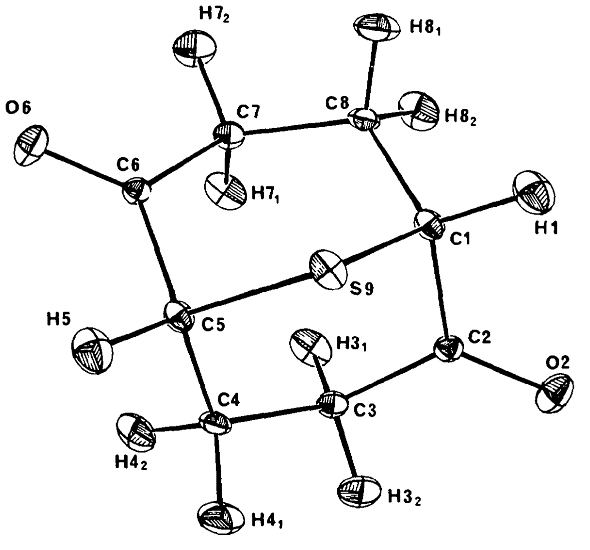

Fig. 1. A general view of the 9-thiabicyclo[3.3.1]nonane-2,6-dione molecule.

The methylene groups at C(3) and C(4) have CCC angles of 115·4 and 117·6°, and HCH angles of 107·3 and 104·6°, respectively. If the HCH angles (2α) and the CCC angles (2φ) are related by simple s,p-hybridization theory, they should comply with the equation $\cot^2\alpha + \cot^2\varphi = 1$ (Coulson, 1948), and on this basis the HCH angles at C(3) and C(4) would be expected to be 104·5 and 103·0°. In the cyclodecane derivative the CCC angles are 113·4–120·1° and the HCH angles 104·7–106·7°. It is clear that CCC angles larger than tetrahedral are associated with HCH angles distinctly smaller than tetrahedral, in accord with the hybridization model; nevertheless, the model does not reproduce the detailed angular variations in these strained molecules and, indeed, could not be expected to do so unless, fortuitously, all the attractive and repulsive forces acting on the atoms were in balance at the calculated angles.

The CCH angles at C(3) and C(4), 106·6–110·8° and 107·2–109·4°, respectively, show that the methylene groups depart slightly from C_{2v} symmetry; the major distortion in each case is a slight bending of the HCH plane out of the CCC bisector (by *ca* 2°), whereas there is no significant bending of the HCH bisector out of the CCC plane at either C(3) or C(4), despite the transannular H···H 3,7-repulsion.

The torsion angles in twin-chair bicyclo[3.3.1]-nonanes with sp^3-hybridized atoms at positions 2, 3, 4, 6, 7 and 8 (Table 6) establish that these molecules distort by displacements of atoms 3 and 7 essentially parallel to the plane through atoms 3, 7 and 9; there is no significant sideways displacement of atoms 3 and 7, with concomitant skewing of the rings. In 9-thiabicyclo[3.3.1]nonane-2,6-dione, on the other hand, the ring torsion angles about bonds 1–2 and 4–5 differ by 15° while those about bonds 2–3 and 3–4 differ by 9°, so that in this case the rings are appreciably skewed. The C(3)···C(7) separation between these skewed rings is 3·18 (1) Å, whereas the corresponding separations in the non-skewed twin-chair compounds

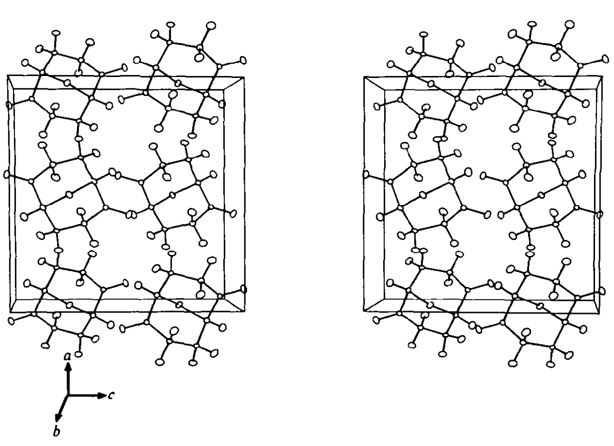

Fig. 2. A stereoscopic view of the molecular packing.

Table 6. *Comparison of torsion angles* (°) *and* 3···7 *separations* (Å) *in various twin-chair bicyclo*[3.3.1]*nonanes*

	A		*B*		*C*		*D*		*E*		Mean	
ω	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	values	*F*
1–2–3–4	−43	−48	−43	−43	−43	−46	−44	−45	−50	−42	45	−47
2–3–4–5	43	48	44	45	42	45	44	44	50	45		38
3–4–5–9	−59	−59	−53	−52	−51	−52	−50	−53	−62	−58	55	−51
3–2–1–9	59	58	50	51	52	55	52	52	62	55		66
2–1–9–5	−67	−59	−61	−61	−62	−64	−62	−62	−67	−61	63	−67
4–5–9–1	68	60	62	61	62	63	60	63	69	60		61
3···7	3·12		3·12, 3·09		3·11		3·06		3·02		3·09	3·18
H(3)···H(7)†	1·93		1·97, 1·97		1·84		1·7–1·8		1·73		–	2·07
H···H(model)‡	1·86		1·88, 1·83		1·86		1·76		1·70		1·82	2·07

A 9-Phenyl-9-phosphabicyclo[3.3.1]nonane (Smith, 1972).
B Bis(9-borabicyclo[3.3.1]nonane) (Brauer & Krüger, 1973).
C 2-Chlorobicyclo[3.3.1]nonan-9-one (Webb & Becker, 1967).
D 1-*p*-Bromobenzenesulphonyloxymethyl-5-methylbicyclo[3.3.1]non-9-ol (Brown, Martin & Sim, 1965).
E 3-Azabicyclo[3.3.1]nonane hydrobromide (Dobler & Dunitz, 1964).
F 9-Thiabicyclo[3.3.1]nonane-2,6-dione.

† The results in this row were derived from the hydrogen coordinates published in the accounts of the X-ray studies. For compound *F*, the neutron result is given.

‡ The results in this row were derived by fitting the 3-methylene geometry of 9-thiabicyclo[3.3.1]nonane-2,6-dione to the carbon skeletons.

are smaller, 3·02–3·12, mean 3·09 Å. The electron-diffraction investigation of bicyclo[3.3.1]nonane yielded a value of 3·10 Å for the C(3)···C(7) distance in the non-skewed parent hydrocarbon. These results indicate that the skewing of the rings in 9-thiabicyclo[3.3.1]nonane-2,6-dione decreases the repulsion between the C(3), C(7) methylene groups.

The X-ray studies of twin-chair bicyclo[3.3.1]nonanes have dealt with the H atoms in several ways; they have been variously ignored, placed in ideal positions, located in difference maps, and adjusted in the least-squares calculations. The results thus obtained for the H···H 3,7-separation range from 1·7 to 2·0 Å and a considerable measure of uncertainty is associated with each value. Our neutron diffraction study establishes that the $H(3_1)\cdots H(7_1)$ separation in 9-thiabicyclo[3.3.1]nonane-2,6-dione is 2·07 (2) Å. Since the bicyclononane derivatives in Table 6 have C(3)···C(7) separations shorter by *ca* 0·1 Å than the separation in the thia compound, it is evident that the H···H 3,7-distances in these compounds must be shorter than 2·07 Å, possibly in the range 1·9–2·0 Å. To obtain a consistent set of estimates for this key distance we adopted the geometry of the C(3) methylene group in 9-thiabicyclo[3.3.1]nonane-2,6-dione as a standard feature to be transferred to the other bicyclononanes and on this basis we calculated that the non-skewed compounds might have H···H separations 1·70–1·88, mean 1·82 Å; if the two earliest, least reliable, structure determinations are omitted these estimates become 1·83–1·88, mean 1·86 Å. The value of 1·86 Å must be regarded as a lower limit for the H···H 3,7-separation in non-skewed twin-chair bicyclononanes, since repulsive interactions will inevitably distort the methylene groups further and increase the H···H distance.

Though the force fields employed in molecular-mechanics calculations use a range of H···H van der Waals potential functions, it appears that the minimum-energy conformation of cyclodecane is not reproduced by potentials in excess of *ca* 5·4 kJ mol^{-1} at 2 Å (White & Bovill, 1976). The force field developed by Allinger incorporates a harder H···H potential and calculations with his field yield an H···H 3,7-separation in bicyclo[3.3.1]nonane of 2·20 Å (Allinger, Tribble, Miller & Wertz, 1971). On the other hand, with the softer H···H potential ($V = 4{\cdot}5$ kJ mol^{-1} at 2 Å) advocated by White & Bovill (1976), which reproduces the short transannular H···H separations in 1,6-cyclodecanediol to within 0·01 Å, the H···H 3,7-separation in bicyclo[3.3.1]nonane is predicted to be 1·97 Å; moreover, the enthalpy difference between the twin-chair and boat–chair conformations is calculated to be 12·1 kJ mol^{-1}, in excellent agreement with the experimental result of *ca* 13 kJ mol^{-1}, whereas the value estimated by Allinger, Tribble, Miller & Wertz (1971) is 6·4 kJ mol^{-1}. Allinger (1977) has recently reported an improved version of his force field, with a softer H···H potential, and calculations based on this yield 2·02 Å for the H···H 3,7-separation in bicyclo[3.3.1]nonane.

1-Methyl-7-*exo-tert*-butylbicyclo[3.3.1]nonane-2,9-dione (Hickmott, Cox & Sim, 1974) provides an interesting alternative test of the proposed H···H potentials, for in this case we can ask whether a soft potential is compatible with the observed boat–chair conformation. Accordingly, we have extended the force field developed by White & Bovill (1976, 1977) to allow for the carbonyl function and carried out calculations for both conformations of the dione which indicate that the boat–chair conformation is indeed of lower energy, by 1·4 kJ mol^{-1}. The adoption of the boat chair conformation in this molecule can be attributed largely to effects arising from the carbonyl groups since our calculations indicate that the boat–chair conformation is also preferred in 1-methylbicyclo[3.3.1]nonane-2,9-dione, though only to the extent of 0·8 kJ mol^{-1}, whereas the twin-chair conformation is favoured by 3·3 kJ mol^{-1} in 1-methyl-7-*exo*-*tert*-butylbicyclo[3.3.1]-nonan-9-one and by 7·9 kJ mol^{-1} in 1-methyl-7-*exo*-*tert*-butylbicyclo[3.3.1]nonane. Since the enthalpy difference in favour of the twin-chair conformation in 1-methylbicyclo[3.3.1]nonane is calculated to be 11·4 kJ mol^{-1} (*cf.* 12·1 kJ mol^{-1} in bicyclo[3.3.1]nonane), the buttressing effect of a 7-*exo*-*tert*-butyl substituent should be much smaller in bicyclo[3.3.1]nonane-2,9-dione than in the parent hydrocarbon.

In order to perform molecular-mechanics calculations for 9-thiabicyclo[3.3.1]nonane-2,6-dione, additional parameters have to be introduced for the S atom. Allinger & Hickey (1975) have investigated the calculation of energies and structures of thiaalkanes and deduced a set of parameters for S that gave good results for a range of simple alkane derivatives and cyclic compounds. They chose, for simplicity, to treat the S atom as spherical but noted that it might be necessary in some molecules to allow for the lone pairs of electrons. For calculations on 9-thiabicyclo[3.3.1]-nonane-2,6-dione we initially adopted parameters equivalent to those reported by Allinger & Hickey (1975) and obtained an optimized molecular geometry in which the six-membered rings were not skewed as found in our neutron and X-ray diffraction studies. Moreover, with this force field we estimated that the twin-chair conformation of 9-oxa-3,7-dithiabicyclo-[3.3.1]nonane should be of lower energy, by 18·4 kJ mol^{-1}, than the boat–chair conformation, whereas only the latter conformation has been observed (Zefirov, Rogozina, Kurkutova, Goncharov & Belov, 1974). In view of these results, we adjusted the force-field parameters in attempts to reproduce both the boat–chair preference in 9-oxa-3,7-dithiabicyclo[3.3.1]nonane and the skewing of the rings in 9-thiabicyclo[3.3.1]nonane-2,6-dione. An increase in the van der Waals parameter r^* for S, leading to increased S$\cdots$S and S$\cdots$H repulsions, improved the situation. Our final choice of parameters gave $\omega(9-1-2-3) = 66{\cdot}0°$ and $\omega(3-4-5-9) = -50{\cdot}3°$ (*cf.* experimental results 66·1 and −51·0°) as a measure of the skew in 9-thiabicyclo[3.3.1]nonane-2,6-dione and predicted the H$\cdots$H 3,7-separation in the molecule to be 2·11 Å (*cf.* experimental result 2·07 Å). The enthalpy difference in favour of the twin-chair conformation of 9-oxa-3,7-dithiabicyclo[3.3.1]nonane was reduced to 11·3 kJ mol^{-1}. The inability to obtain more satisfactory results suggests that it may be necessary to allow explicitly for S$\cdots$S lone-pair repulsion in 9-oxa-3,7-dithiabicyclo-[3.3.1]nonane and possibly also for S lone-pair $\cdots$axial—H(4) repulsion in 9-thiabicyclo[3.3.1]-nonane-2,6-dione. However, such additional parameterization of the force field would only be reliable if based on a greater number of experimental results.

APPENDIX

The steric energy (E_s) of a molecule is represented as the sum of contributions from each of the terms describing potential energy as a function of molecular deformations from an arbitrary reference geometry:

$$\begin{aligned} E_s = {} & \sum_l \tfrac{1}{2}k_l(l-l_0)^2 + \sum_\theta \tfrac{1}{2}k_\theta(\Delta\theta^2 - k'_\theta\,\Delta\theta^3) \\ & + \sum_\omega \tfrac{1}{2}k_\omega(1 + s\cos n\omega) \\ & + \sum_r \varepsilon\{-2/\alpha^6 + \exp[12(1-\alpha)]\} \\ & + \sum_\chi \tfrac{1}{2}k_\chi\,(180-\chi)^2. \end{aligned}$$

Here l, θ, r and ω are bond lengths, bond angles, 1—4 and higher interatomic distances and torsion angles, respectively. Also, $\alpha = r/(r_1^* + r_2^*)$ and $\Delta\theta = \theta - \theta_0$. The values of the force constants k_l, k_θ, k'_θ, k_ω, ε, k_χ, and the equilibrium geometry parameters l_0, θ_0, s, n and r^* were taken from the compilation of White & Bovill (1977) supplemented by the values shown in the Supplementary Publication.†

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† See previous footnote.

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The Crystal and Molecular Structure of the Neuroleptic Pimozide Hydrochloride, 1-{1-[4,4-bis(4-fluorophenyl)butyl]-4-piperidyl}-2-benzimidazolinone HCl

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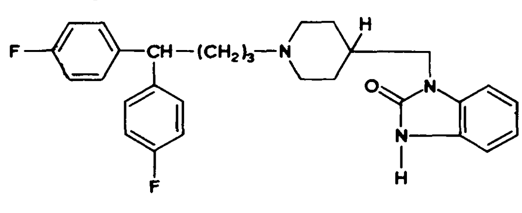
Abstract

Crystals of pimozide, $C_{28}H_{29}F_2N_3O.HCl$, are monoclinic, space group $P2_1/c$ with unit-cell dimensions a = 10·007 (3), b = 25·880 (9), c = 10·014 (4) Å, β = 99·15 (7)°, Z = 4. The crystal structure was analysed by the heavy-atom method and refined by full-matrix least-squares calculations to a final R of 0·046.

Introduction

Pimozide, $C_{28}H_{29}F_2N_3O.HCl$ (R24970; pimozide base: R6238; pimozide HBr: R24969) is a neuroleptic (major tranquillizer) drug with anticholinergic activity. As part of a systematic study of substances affecting the peripheral and central nervous systems, the crystal structure of pimozide HCl was analyzed.



Experimental

Crystals of pimozide hydrochloride (R24970) obtained from Janssen Laboratories, grown from a saturated solution of methanol and water (4:1) at 313

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