# Half-Chair Conformations of Unsaturated Heterocyclic Compounds

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The vicinal proton coupling constants were obtained for some 6-membered ring unsaturated heterocyclic compounds. The R values and ring dihedral angles were determined and found to be consistent with half-chair conformations. Relative to saturated heterocyclic compounds, the effect of the sulfur atom on ring puckering was attenuated. However, an increase in ring puckering resulted from the sulfone group and was attributed to torsional energy.

# **INTRODUCTION**

A cis and trans vicinal proton coupling constant,  $J_c$  and  $J_t$ , may be obtained from the NMR spectrum of the X—CH<sub>2</sub>CH<sub>2</sub>—Y fragment in cyclic compounds that are averaged by rapid conformational interconversion (1).



The magnitude of the vicinal coupling constant ratio, R, has been shown to be a measure of ring geometry and independent of the electronegativities of the attached atoms X and Y.<sup>1,2</sup> Relative to cyclohexane the bismethylene fragments may be undistorted, flattened, or puckered, which will result in values of R between 1.9 and 2.2, less than 1.9 or greater than 2.2, respectively.<sup>1,2</sup>

The ring dihedral angle,  $\theta$ , in 6-membered rings may be determined from the value of R.



Equation (2) was obtained by  $Buys^2$  after expressing the coupling constants in terms of the Karplus equation and making the approximation of trigonal projection symmetry.

$$\cos\theta = \left[\frac{3}{4R+2}\right]^{1/2} \tag{2}$$

The ring dihedral angles for the undistorted chair 6-membered rings have values of  $\theta$  from 56° to 58°,

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while that for the flattened ring is less, and the value of  $\theta$  for a puckered ring is greater.<sup>1,2</sup>

While the application of the R value technique to saturated 6-membered heterocyclic rings is well established, we wish to report the results of an application to 6-membered ring heterocyclic compounds A and B, containing endocyclic or benzo carbon-carbon double bonds, which are listed in Table 1.



## **RESULTS AND DISCUSSION**

The unsymmetrically substituted compounds, or those for which atoms X and Y were different, resulted in AA'BB' spectra which were first analyzed by hand;<sup>3,4</sup> the resulting parameters were then refined by iterative

#### Table 1. Heterocyclic compounds studied

Compound	×	Y	R	R'	
1	0	0	н	н	
2	0	0	Cl	н	
3	0	0	C <sub>6</sub> H₅	C <sub>6</sub> H₅	
4	0	0	be	nzo	
5	S	0	н	н	
6	S	0	CI	н	
7	S	0	C <sub>6</sub> H₅	C₅H₅	
8	S	0	benzo		
9	SO2	0	benzo		
10	S	S	н	н	
11	S	S	C <sub>6</sub> H₅	C <sub>6</sub> H₅	
12	S	S	benzo		
13	S	S	6-methylbenzo		
14	0	NH	benzo		
15	S	NH	benzo		
16	SO₂	NH	benzo		
17	CH₂	S	benzo		
17a	$CD_2$	S	benzo		
18	CH₂	SO₂	benzo		
18a	$CD_2$	SO₂	benzo		
19	C==0	S	be	nzo	
20	C==0	SO₂	benzo		

analysis using LAOCN 3. While analysis of a spectrum yielded the vicinal coupling constants, it was not usually possible to obtain the geminal coupling constants, since the spectrum was generally insensitive to the sum of J(AA') and J(BB'). In this case dummy coupling constants were chosen (c.-11 to -13 Hz), so the difference between J(AA') and J(BB') was that obtained from the hand analysis.

In the cases of 2,3-dihydro-4H-1-benzothiopyran (17) and sulfone (18), the virtual coupling arising from the 4-methylene resulted in broad lines for the 2- and 3-methylene resonances. Thus, it was necessary to deuterate this position, 17a and 18a, in order to obtain readily analyzable spectra for these compounds.

In the spectra of compounds in which atoms X and Y were the same and were also symmetrically substituted, the protons of the bismethylene group were equivalent and gave rise to a single resonance. In these compounds the vicinal coupling constants were obtained from the proton <sup>13</sup>C satellite spectrum by analysis as an AA'XX' spectrum.

The 100 MHz <sup>1</sup>H NMR spectrum of the bismethylene fragment of 6-methyl-2,3-dihydro-1,4benzodithiin (13) in a variety of solvents always showed only a single resonance. The spectrum of a neat sample gave a single line of  $W_2^1 = 1.1$  Hz with three very weak high field lines and, symmetrically disposed to the intense center peak, three very weak lines to low field. However, in order to extract the vicinal coupling constants, it was necessary to determine the <sup>13</sup>C satellite spectrum of the bismethylene protons, which consisted of two overlapping five line patterns of 2:1:2:1:2 intensity ratio to low field of the center resonance and the mirror image to higher field. The two multiplets were analyzed as two AA'XX' spectra and each yielded the same values for J(AX)and J(AX') of 7.97 Hz and 3.31 Hz, respectively. If the <sup>13</sup>C—<sup>1</sup>H coupling constant for each methylene group is the same, then the difference between the center of the two overlapping five line patterns of 2.08 Hz will equal the chemical shift difference between the two methylene groups in compound 13. Using vicinal coupling constants and the chemical shift difference between the methylene groups obtained from the <sup>13</sup>C satellite spectrum, and assuming the geminal coupling constants J(AA') and J(BB') to have a value of -13.0 Hz, the spectrum of the bismethylene protons was calculated using LAOCN 3. The low field <sup>13</sup>C satellite and the bismethylene proton spectra of **13** are shown in Fig. 1. The <sup>1</sup>H NMR parameters, Rvalues, and XCCY dihedral angles for heterocyclic compounds 1-20 are summarized in Table 2.

The molecular geometry of cyclohexene has been well studied,<sup>2,10,11,12</sup> with the conclusion that the conformation of cyclohexene is half-chair with an R value of 3.03 and a C-3, C-4, C-5, C-6 ring dihedral angle of 63°. The structure of 2,3-dihydro-1,4-dioxin (1) has been the subject of microwave<sup>13</sup> and <sup>1</sup>H NMR<sup>5,14</sup> studies with the conclusion that 1 exists in a half-chair conformation very similar to that of cyclohexene, but slightly flattened. An R value of 2.73 and an OCCO dihedral angle of 61° was calculated from the low temperature <sup>1</sup>H NMR coupling constants,<sup>5</sup> which compares favorably with our R value of 2.55 and dihedral



**Figure 1.** The 100 MHz proton NMR spectrum of the bismethylene group of 6-methyl-2,3-dihydro-1,4-benzodithiin (13) is shown in plot (a). The calculated spectrum is given in plot (b), in which the center lines between the slashes are plotted at one-tenth the intensity of the outer lines. The low field <sup>13</sup>C satellite spectrum of the bismethylene protons of 13 is shown in plot (c).

angle of 60°.

R values from 2.16 to 3.55, which correspond to XCCY dihedral angles ( $\theta$ ) of 58° to 64°, respectively, were obtained for heterocyclic compounds 1-20 (Table 2). On considering molecular symmetry, the dihedral angles obtained for the dihydrodioxins and the dihydrodithiins are consistent with a half-chair conformation similar to the C<sub>2</sub> symmetric half-chair conformation of cyclohexene. However, the remaining heterocyclic compounds studied (X  $\neq$  Y) have different X—C and C—Y bond distances and CXC and CYC bond angles. Thus, although the values of  $\theta$  determined for these compounds are similar to that of cyclohexene, the conformations may be significantly perturbed from a cyclohexene type half-chair conformation.

In order to investigate ring conformation effects of substituents on the  $sp^2$  hybrid carbon atoms, substituted dihydrodioxins 2 and 3, dihydro-oxathiins 6 and 7, and dihydrodithiin 11, and their benzo analogs 4, 8, 12, and 13 were examined. No significant differences in R values or  $\theta$  were found between the unsubstituted and the 2-chloro- or 2,3-diphenyl- substituted compounds 2, 6, 3, and 7, or the dihydrobenzodioxin 4 and dihydrobenzoxathiin 8. However, dihydrobenzodithins 12 and 13, with R values of 2.4 and  $\theta$  of 59°. show significant flattening of the half-chair conformation relative to dihydrothiin 10 with values of R and  $\theta$ of 3.50 and 64°. While the origin of the ring flattening effect is not understood, it is consistent with an increase in one or more ring bond angles. An increase in the CSC angle might be expected if one considers that the CSC angle of  $98.9^{\circ}$  of dimethyl sulfide<sup>15</sup> increased to  $105.6^{\circ}$  in methylthiobenzene<sup>16</sup>, has but methylthioethene<sup>17</sup> has a CSC angle of 104.5°.

	Compound		δAB(ppm)	J,ª(Hz)	J <sub>c</sub> <sup>b</sup> (Hz)	$\Delta J_{gem}(Hz)$	R	XCCY angle (θ, degrees) <sup>e</sup>
R' 0.	R = H, R' = H	(1)		5.62	2.20		2.55	60(61 <sup>d</sup> )
	$\mathbf{R} = \mathbf{C}\mathbf{I}, \mathbf{R}' = \mathbf{H}$	(2)	0.15	5.61	2.27	(-11.22-11.45)°	2.47	60
	$\mathbf{R} = \mathbf{C}_{\mathbf{e}}\mathbf{H}_{\mathbf{e}}, \ \mathbf{R}' = \mathbf{C}_{\mathbf{e}}\mathbf{H}_{\mathbf{e}}$	(3)		5.34	2.23		2.39	59
R	benzo	(4)		5.77	2.28		2.53	60
R'S	R = H, R' = H	(5) <sup>6</sup>	1.35	6.8	2.1	2.1	3.1	63
Ύ)	R = CI, R' = H	(6)	1.14	6.85	2.22	2.1	3.08	63
	$R = C_6 H_5, R' = C_6 H_5$	(7)	1.30	6.75	2.32	2.1	2.91	62
R	benzo	(8)	1.29	7.00	2.40	1.7	2.92	62
SO <sub>2</sub>		(9)	1.30	8.37	2.51	1.3	3.33	64
B' C	R = H. R' = H	(10)		10.26	2.93		3.50	64
"\_">	$R = C_0 H_e$ , $R' = C_0 H_e$	(11)		7.91	2.23		3.55	64
	benzo	(12)		7.99	3.33		2.40	59
R S	6-methylbenzo	(13)	0.02	7.97	3.31	0.0	2.41	59
	X ≔ O, Y = NH	(14)	0.88	6.13	2.68	(-13.24-12.25)°	2.29	59
	X = S, Y = NH	(15)	0.53	7.20	2.86	(11.48-11.95)°	2.52	60
$\checkmark$	$X = SO_2, Y = NH$	(16)	0.61	8.80	3.14	0.0	2.80	62
	$X = CD_2, Y = S$	(17a)	0.88	8.20	3.70	1.28	2.22	58
	$X = CD_2, Y = SO_2$	(18a)	0.81	9.16	3.25	0.90	2.82	62
·	X = C=0, Y = S	( <b>19</b> ) <sup>7</sup>		9.44	3.45		2.73	61
	$X = C = 0, Y = SO_2$	( <b>20</b> ) <sup>7</sup>		8.92	4.14		2.16	58

Table 2. <sup>1</sup>H NMR and conformational parameters

<sup>a</sup> J(AB').

<sup>▶</sup> J(AB).

<sup>c</sup> J(AA') and J(BB'), respectively.

<sup>d</sup> This compares favorably with a value of  $\theta = 61^{\circ}$  calculated from values of  $J_{aa}$ ,  $J_{ae}$ , and  $J_{ee}$  from the low temperature NMR study<sup>5</sup> of 1. <sup>e</sup> Using  $J_c$  and the electronegativities<sup>6</sup> of X and Y, the values of  $\theta$  calculated according to Forrest<sup>9</sup> generally agreed with  $\theta$  obtained from the *R* value. However, in cases where a change in  $J_c$  is also accompanied by a proportional change in  $J_t$  which leaves *R* unchanged, as in **10** and **11**, the values of  $\theta$  derived from  $J_c$  and electronegativities do not agree with the *R* value results. For **10** and **11**  $J_c$  and electronegativities yield values of  $\theta$  equal to 63° and 67°, respectively.

A comparison of ring geometries of several unsaturated heterocyclic compounds and their saturated analogs is collected in Table 3. The effect of the endocyclic carbon-carbon double bond of cyclohexene is to increase the *R* value and the ring dihedral angle to 3.03 and  $63^{\circ 2}$  from 2.16 and  $58^{\circ 1,2}$  for cyclohexane, respectively. Relative to 1,4-dioxane, the O--CH<sub>2</sub>CH<sub>2</sub>--O dihedral angle of 2,3-dihydro-1,4dioxin (1) has only increased 2-3° from 58° to 60° or 61°. In addition, the other unsaturated heterocyclic compounds exhibit no significant change in the XCH<sub>2</sub>CH<sub>2</sub>Y dihedral angle relative to their saturated analogs.

Unlike the 3- and 6-methylene groups of cyclohexene, the heteroatom nonbonding electrons may have significant 2p-2p or  $3p-2p \pi$  interactions with the carbon double bond or the benzene  $\pi$  systems. The COC angle in dimethyl ether  $(111^\circ)^{18}$  increases in anisole  $(120^\circ)^{19}$  and methyl vinyl ether  $(120^\circ)^{20}$  and the CSC angle in dimethyl mercaptan  $(98.9^\circ)^{15}$  increases in methylthiobenzene  $(105.6^\circ)^{16}$  and methylthioethene  $(104.5)^{.17}$  Thus, at least some increase in the CXC angle is expected for the unsaturated compounds relative to the CXC angles in the saturated analogs. The increase in the CXC angles would result in ring flattening and is consistent with the observed attenuation of the puckering effect of the carbon double bond from that observed for cyclohexene.

It can also be noted in Tables 2 and 3 that while the substitution of a sulfur atom in the ring does generally

Table 3.	Comparison	of R value	and XCCY	angle, 0, for
	saturated an	nd analogous	unsaturated	heterocyclic
	compounds			

$ \begin{pmatrix} X \\ Y \end{pmatrix}^{1,2} \begin{pmatrix} X \\ Y \end{pmatrix} $							
х	Y	x	Y	J <sub>t</sub> (Hz)	J <sub>c</sub> (Hz)	R	XCCY Angle (θ, degrees)
CH2	СН,			8.07	3.73	2.16	58
-	-	$CH_2$	CH <sub>2</sub> <sup>2</sup>	8.94	2.95	3.03	63
0	0	-	-	6.11	2.78	2.20	58
		0	O (1)	5.62	2.20	2.55	60 (61 <sup>b</sup> )
0	S			7.63	2.68	2.85	62
		0	S (5) <sup>6</sup>	6.80	2.10	3.10	63
S	S			8.15	2.25	3.62	65
		S	S (10)	10.26	2.93	3.50	64
S	CH₂			8.47	3.28	2.58	60
		S	CD2 <sup>a</sup> (17a)	8.20	3.70	2.22	58

\* The benzo compound.

<sup>b</sup> Calculated from the coupling constants reported in Ref. 5.

result in a puckering of the ring conformations of the unsaturated heterocyclic compounds, the puckering effect is less than that observed for chair conformations of saturated heterocyclic compounds. This is probably due to the restriction on molecular geometry imposed by the requirement of coplanarity of the S-C=C-X group and the long C-S-C bond distances.

Oxidation of dihydrobenzoxathiin (8), dihydrobenzothiazine (15), and thiochroman (17) to their corresponding sulfones 9, 16 and 18 resulted in a puckering of their conformations, rather than the expected flattening of the ring which, for example, is observed for the chair conformation of *trans*-hexahydro-1,4-benzoxathiane 1,1-dioxide (21).<sup>21</sup> The conformation of 2,3dihydrobenzothiopyran-4-one 1,1-dioxide (20), which has been reported by Lambert,<sup>7</sup> also exhibits a ring flattening relative to 2,3-dihydrobenzothiopyran-4one (19).

Since the minimum energy molecular conformation is the result of a number of contributing factors, the origins of small changes in conformation can be elusive. However, the effect of the sulfone group on the half-chair conformation can be qualitatively accounted for by considering torsional and electrostatic energies as the major contributors to conformational changes. An inspection of Dreiding models reveals that the longer carbon–sulfur bond length results in a distorted half-chair conformation, with the 2-methylene slightly out of plane containing the S—C=C—X group and on the same side as the 3-methylene group, and the pseudo-axial hydrogen of the 3-methylene over the ring.



The largest puckering effect was exhibited by sulfone (18), for which electrostatic effects are negligible. Estimates, utilizing Dreiding models, of the *cis*-1,3-sulfone oxygen-hydrogen and sulfone oxygen-*peri*-hydrogen van der Waals energies<sup>22,23</sup> were found to be negligible. In addition, since the CSC angle of  $105.6^{\circ}$  of methylthiobenzene<sup>16</sup> increases to  $112^{\circ}$  in methyl-thiobenzene dioxide,<sup>22</sup> conformational energy minimization in sulfone 18 might result in an increase in the CSC angle. This, however, would lead to ring flattening rather than the observed puckering effect.

In sulfone 18, the 2-methylene and the sulfone are nearly eclipsed and near a torsional energy maximum which would be relieved by ring puckering. The conformation of benzothiopyran (17) is similar to 18. However, if the methyl torsional barriers for dimethyl sulfone<sup>25</sup> and dimethyl sulfide<sup>15</sup> of 4.2 kcal mol<sup>-1</sup> and 2.1 kcal mol<sup>-1</sup>, respectively, are considered, the torsional energy relief gained by ring puckering is less for 17 than the sulfone 18. Thus, due to the larger torsional energy for the eclipsed methylene and sulfone groups, ring puckering rather than ring flattening results. In contrast, the hexahydrobenzoxathiane sulfone 21 has the sulfone and 2-methylene groups in a staggered conformation, which is at a torsional energy minimum. The ring flattening observed for sulfone 21 has been attributed to nonbonded energy minimization.<sup>21</sup>

While ring conformations of 8, 9, 15 and 16 are similar to those of 17 and 18, the sulfone puckering effect is not as large for the dihydrobenzoxathiin sulfone 9 and dihydrobenzothiazine sulfone 16 as for the sulfone 18. Ring puckering not only increases the sulfone 2-methylene dihedral angle, but also decreases the distance between the sulfur and 3-carbon atoms which results in a larger electrostatic energy. Thus, the ring puckering experienced by sulfones 9 and 16 is attenuated by electrostatic effects.

Finally, the electrostatic energy may be the dominant factor in the ring flattening observed for 2,3dihydrobenzothiopyran-4-one 1,1-dioxide (20) relative to benzothiopyran-4-one (19). While ring conformations of 19 and 20 are similar to 17 and 18, ring puckering would increase the electrostatic energy between the sulfone and carbonyl group of 20. However, ring flattening would minimize this interaction.

The R value technique has been applied to a number of unsaturated heterocyclic compounds, and the results are consistent with the compounds being in a half-chair conformation. For the unsaturated heterocyclic compounds which were studied, the endocyclic carbon-carbon double bond and the sulfur atom in the ring attenuated the puckering effects observed for cyclohexene and the analogous saturated sulfur heterocyclic compounds. The effect of the sulfone group was accounted for by consideration of torsional and electrostatic energies. Finally, these results provide a basis to study the conformations of substituted unsaturated heterocyclic compounds.

## **EXPERIMENTAL**

All melting points were determined using a Thomas Hoover apparatus and are uncorrected. The infrared spectra were determined on a Perkin–Elmer 337 spectrometer as a neat smear or a KBr pellet. Elemental analyses were done by Mr James Cress using a Hewlett–Packard 185 CHN analyzer or were obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee, USA.

Proton NMR spectra were recorded using 10% w/w CDCl<sub>3</sub> solutions which contained c. 3% TMS and had been degassed under vacuum by the freeze-thaw method. The proton <sup>13</sup>C satellite spectra were determined using neat samples of liquids or saturated solutions of solid compounds in CDCl<sub>3</sub> or acetone- $d_6$ . Frequency sweep <sup>1</sup>H NMR spectra were obtained at 60 MHz or 100 MHz using a Perkin-Elmer R-20 or a Varian HA-100 spectrometer. A sweep rate no faster than 0.1 Hz s<sup>-1</sup> was utilized. The spectra were calibrated to  $\pm 0.1$  Hz using a Hewlett-Packard frequency counter. The line positions are an average of four traces of the spectrum, with a standard deviation of the differences in line position of less than 0.06 Hz. Analysis of the spectra was accomplished with the aid

of LAOCN 3 and a CDC 3150 computer. The fit between the calculated and experimental spectrum was considered satisfactory when the RMS deviation between them was less than 0.10 Hz.

Literature procedures were followed in order to accomplish the synthesis of heterocyclic compounds:  $1,^{26-28}$   $2,^{26,27}$   $3,^{30}$   $4,^{31}$   $6,^{6}$   $7,^{32}$   $8,^{33,34}$   $9,^{34}$   $10,^{35}$   $12,^{36,37}$  $13,^{38}$   $14,^{39}$   $15,^{40}$   $17,^{41,42}$   $17a^{41}$  and  $18,^{43}$  The identity of each compound was verified by its <sup>1</sup>H NMR spectrum.

# 5,6-Diphenyl-2,3-dihydro-1,4-dithiin (11)

A solution of 21.2 g (0.1 mol) of benzoin, 9.4 g (0.1 mol) of 1,2-dimercaptoethane, 0.25 g of ptoluenesulfonic acid and 150 ml of toluene were refluxed overnight using a Dean Stark trap. After removing the toluene under reduced pressure, the residue was chromatographed on 250 g of alumina, eluting with 2 litres of hexane and 1 litre of 1:3 benzene-hexane. The last 1.5 litres of eluant was collected and the solvent removed under reduced pressure. The residue was recrystallized from methanol to give 4.0 g of **11**, m.p. 102–103 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.04 (s, 10H) and 3.30 ppm (s, 4H). Analysis calculated for C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>: C, 71.60; H, 4.52;

found: C, 71.65; H, 4.80.

#### 3,4-Dihydro-2H-1,4-benzothiazine 1,1-dioxide (16)

To a solution of 2.25 g (11 mmol) of 3-oxo-3,4dihydro-2H(4H)-1,4-benzothiazine 1,1-dioxide<sup>40</sup> in 75 ml of THF was added an excess of a 1 M diborane THF solution. After the reaction mixture had been stirred overnight, 60 ml of 10% HCl were added and the resulting mixture concentrated to one quarter of its volume. The mixture was made alkaline with 10% NaOH and extracted twice with chloroform. The chloroform solution was washed with water, dried over  $MgSO_4$ , and filtered. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give 1.53 g of 16, m.p. 142-143 °C; IR (KBr) 3370 (NH), 1280 (SO<sub>2</sub>), 1125 cm<sup>-1</sup> (SO<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.9–6.5 (m, 4H), 4.65 (s, 1H, exchanged with D<sub>2</sub>O), 3.90 (AA', 2H) and 3.28 ppm (BB', 2H).

Analysis—calculated for C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 52.30; H, 5.05; N, 7.57; found: C, 52.44; H, 4.95; N, 7.64.

## 2,3-Dihydro-4H-1-benzothiopyran 1,1-dioxide-4,4-d<sub>2</sub> (18a)

After 2,3-dihydro-4H-1-benzothiopyran-4,4- $d_2$  (17a) had been prepared according to a reported procedure,<sup>41</sup> it was oxidized utilizing the same procedure<sup>4</sup> used for the oxidation of **17** to **18**, which yielded **18a**; IR (KBr) 1280 (SO<sub>2</sub>), 1135 cm<sup>-1</sup> (SO<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.86–7.04 (m, 4H), 3.26 (m, 2H), 2.42 ppm (m, 2H) and the 4-methylene multiplet present for 18 was absent.

## Acknowledgments

We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Department of Chemistry, University of California, Davis, for the generous gift of the Varian HA-100 spectrometer.

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Received 16 April 1981; accepted (revised) 18 September 1981 © Heyden & Son Ltd, 1982