

## Conformational Study of Substituted Methyl Phenyl Sulphoxides. A Multinuclear ( $^1\text{H}$ , $^{13}\text{C}$ , and $^{17}\text{O}$ ) Approach

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A number of ring-substituted methyl phenyl sulphoxides have been examined with a multinuclear n.m.r. approach in order to obtain experimental evidence of the conformational properties of the methylsulphinyl group bonded to an aromatic ring. Measurements were performed of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{17}\text{O}$  chemical shifts and LIS (lanthanide-induced shifts) on  $^1\text{H}$  and  $^{13}\text{C}$ , long-range  $^{13}\text{C}$ - $^1\text{H}$  coupling constants. Each of these approaches by itself is not fully conclusive in showing the orientation of the SO bond in the different compounds examined, but by using them in combination a sound picture of the conformational behaviour of these molecules in solution can be obtained. The SO bond is thus almost coplanar with the aromatic ring in *ortho*-substituted compounds and oriented in the opposite direction with respect to the substituent. The twist-angle probably differs slightly as a function of the *ortho*-group. An increasing degree of distortion from coplanarity is found in *para*-substituted derivatives and *ortho*-disubstituted compounds. As regards  $^{17}\text{O}$  chemical shifts, these were found to span a smaller range than in the corresponding acetophenones.

The problem of the relative orientation of the SO bond of sulphoxides and of an unsaturated or aromatic system has not yet received as much attention as that devoted to carbonyl compounds.<sup>1</sup> Owing to the pyramidal structure of the sulphanyl group, the energy profile for rotation around the  $\text{C}_{\text{ar}}\text{-S}$  bond of methyl phenyl sulphoxides is expected to be more complex than in the case of acetophenones, where the coplanar and perpendicular conformations of the acetyl group with respect to the benzene ring are readily identified with ground and transition states for the internal rotation process. The implication of d-orbitals of sulphur in  $\sigma$  and  $\pi$  bond formation<sup>2</sup> with adjacent (carbon and oxygen) atoms makes it rather difficult to predict the characteristics of ground and transition states for the hindered rotation<sup>3</sup> of the methylsulphinyl group around the  $\text{C}_{\text{ar}}\text{-S}$  bond on an empirical basis. Manifold degeneracy of d-orbitals can enable electronic stabilization of the molecule for several orientations of the SO bond with respect to the aromatic ring.

Recent theoretical results from *ab initio* calculations, reported by some of us,<sup>4</sup> have shown that in methyl phenyl sulphoxide the conformational energy profile has only one energy minimum, fairly flat, corresponding to the SO bond nearly eclipsed (twist-angle from the ring  $7.31^\circ$ ) with the ring carbon atoms and the transition state occurs when the S-Me bond is coplanar with the ring. The ground-state conformation is close to that found<sup>5</sup> for methyl *p*-tolyl sulphoxide in the solid state. Situations near to coplanarity of the SO bond and aromatic ring are also found in *ortho*-substituted derivatives, at least when the substituent is a chlorine atom<sup>6</sup> or a methoxycarbonyl group,<sup>7</sup> and the sulphanyl oxygen points in the direction opposite to the substituent in the ring. A different ground-state conformation has, however, been proposed for the 2-methyl derivative.<sup>8</sup>

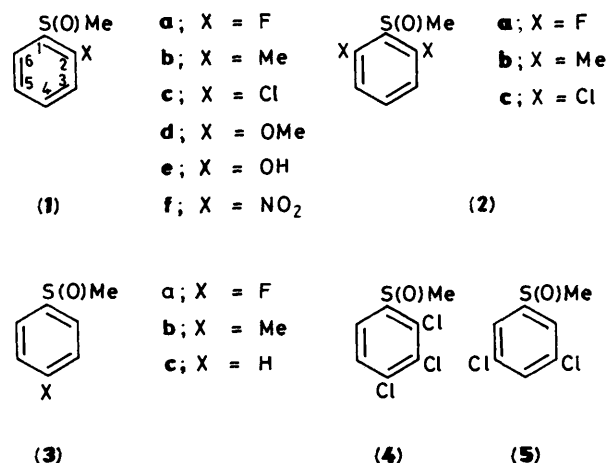
On the other hand, *para* substituents have a negligible effect on the geometrical structure of the preferred conformation, as can be deduced from  $^1\text{H}$  n.m.r. LIS (lanthanide-induced shifts) simulation,<sup>6</sup> X-ray crystallography,<sup>7</sup>  $^{13}\text{C}$  chemical shifts,<sup>8</sup> and Kerr constants.<sup>9</sup>

In this paper we report an experimental study on a number of ring-substituted methyl phenyl sulphoxides with the aim of acquiring more knowledge about the conformational behaviour of the methylsulphinyl group bonded to an aromatic ring.

Different approaches will be employed based on multinuclear n.m.r. measurements of  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{17}\text{O}$ , including LIS simulation<sup>10</sup> on the former two nuclei and long-range  $^n\text{J}(\text{C-H})$  coupling constants involving the  $^{13}\text{C}$  nucleus of the methylsulphinyl group.

### Results and Discussion

The molecules chosen for examining the conformational behaviour of the methylsulphinyl group bonded to the phenyl ring are (1)–(5). Compounds containing one and two substituents



in *ortho* positions were selected for a study of the substituent effect on the orientation of the SO bond, while a number of derivatives differently substituted in the ring should contribute to our knowledge of the dependence of experimental observables on substituent electronic effects when minor changes of conformation occur.

*Results from N.M.R. LIS Measurements.*—The  $^1\text{H}$  and  $^{13}\text{C}$  LIS values for a number of representative compounds are

**Table 1.** LIS values  $\Delta M$  (p.p.m.) due to  $\text{Yb}(\text{fod})_3$  on  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for a number of derivatives. Those for  $^{13}\text{C}$  were corrected ( $\Delta M - \Delta D$ ) for the complexation shift in the presence of  $\text{La}(\text{fod})_3$ .

Compound		C-1	C-2	C-3	C-4	C-5	C-6	$\text{SOCH}_3$	2-H	3-H	4-H	5-H	6-H	$\text{SOCH}_3$
(1a)	$\Delta M$	35.89	18.54	10.38	9.77	12.46	33.82	39.25		6.03	5.69	7.03	43.75	29.75
	$\Delta M - \Delta D$	41.55	18.54	10.38	9.77	12.46	31.64	42.45						
(1b)	$\Delta M$	34.00	18.34	10.59	10.07	13.32	33.53	41.04		6.95	5.15	7.93	40.05	29.64
	$\Delta M - \Delta D$	39.37	18.34	10.59	10.07	13.32	31.37	44.24						
(1c)	$\Delta M$	34.50	18.04	10.32	9.85	12.85	33.87	39.50		6.32	5.70	6.53	47.58	29.87
	$\Delta M - \Delta D$	40.48	18.04	10.32	9.85	12.85	31.85	42.73						
(2a)	$\Delta M$	28.36	22.02	11.13	9.72	11.13	22.02	34.56		7.12	6.33	7.12		24.62
	$\Delta M - \Delta D$	33.77	21.16	11.13	8.87	11.13	21.16	37.68						
(2c)	$\Delta M$	36.32	26.15	12.84	10.84	12.84	26.15	41.69		8.18	7.03	8.18		30.11
	$\Delta M - \Delta D$	40.72	25.29	12.84	10.84	12.84	25.29	44.39						
(3b)	$\Delta M$	32.03	23.40	10.65	9.37	10.65	23.40	37.42	25.30	6.45		6.45	25.30	27.65
	$\Delta M - \Delta D$	37.47	22.54	10.65	8.62	10.65	22.54	40.50						

**Table 2.** Results of LIS simulation: molecular geometry parameters for the complexes<sup>a</sup> and conformational angle<sup>b</sup>  $\theta$  for a number of representative compounds.

Compound	$R_{\text{cryst}}$	$R/\text{\AA}$	$\varphi$	$\psi$	Population <i>endo</i>	Twist-angle ( $^\circ$ )
(1a)	0.029	3.35	45	135	10	30 $^\circ$
(1b)	0.020	3.45	40	130	5	30 $^\circ$
(1c)	0.022	3.40	45	130	10	10 $^\circ$
(2b)	0.020	3.20	85	115	5	40–90
(2c)	0.006	3.35	60	120	5	40–90
(3b)	0.013	3.45	35	135	5	40 $^\circ$

<sup>a</sup> For the symbols see ref. 10. <sup>b</sup> Defined in the Figure. <sup>c</sup>  $\pm 10^\circ$ .

reported in Table 1. From the  $\Delta M$  shifts caused by  $\text{Yb}(\text{fod})_3$ ,\* the  $^{13}\text{C}$  diamagnetic complexation shift  $\Delta D$  obtained in the presence of  $\text{La}(\text{fod})_3$  was subtracted.<sup>10</sup> The LIRAS-3 computer program<sup>10</sup> was employed in the 'four-site' axially symmetric complexation model for processing of the experimental LIS values. The results are collected in Table 2, where the symbolism is the same as that used in previous work.<sup>10,11</sup> The twist-angles  $\theta$  reported in Table 2 correspond to the lowest  $R_{\text{cryst}}$  (which indicates the best agreement between calculated and experimental LIS values) for each compound. Minima are well defined for compounds (1) and (3b), whereas they are less well determined in the case of derivatives (2). This higher inaccuracy for the latter compounds is due to the smaller number of measurable LIS values.

The LIS simulation does not distinguish between negative and positive values of  $\theta$ . Even so, negative values should be less probable since they correspond to the methyl group approaching the phenyl ring, and this should correspond to an increase of the molecular energy, according to theory.<sup>4</sup>

In spite of the approximate nature of these results the following information can be derived from LIS measurements. For compounds (1) the angle  $\theta$  spans the conformational region of the coplanar situation of the SO bond and of the phenyl ring (0–30 $^\circ$ ), and it can clearly be seen that the oxygen atom of the SO group is directed *anti* with respect to the *ortho* substituent. This appears also from direct inspection of carbon LIS values in Table 1 (compare C-2 and C-6). This holds for compounds (1d) and (1f) as well, not reported in Table 1. The result relative to compound (1c) agrees with the conclusion of previous work.<sup>6</sup> A range of higher degrees of twist is found for compounds (2) (40–90 $^\circ$ ) and at an intermediate level for derivatives (3) (30–50 $^\circ$ ).

<sup>13</sup>C, <sup>1</sup>H, and <sup>17</sup>O Chemical Shifts.—In the <sup>1</sup>H and <sup>13</sup>C chemical shifts of ring-carbon and -proton nuclei (derived from the spectra and not reported) it is difficult to recognize trends which could help in conformational analysis. Trends which seem to characterize different orientations of the SO bond seem nevertheless to be present in the chemical shifts of the nuclei of the methylsulphonyl group, collected in Table 3.

The <sup>13</sup>C resonances are grouped in three regions: at  $\delta 44.00 \pm 0.05$  for those compounds without *ortho* substituents [(3) and (5)], at  $\delta 41.69 \pm 0.31$  for those with an *ortho* substituent [(1) and (4), but excluding compound (1f)], and at  $\delta 38.78 \pm 0.77$  for those with two *ortho* substituents. As regards the NO<sub>2</sub> group, compound (1f), it is likely that a direct through-space interaction between the sulphur atom and the oxygen atoms of the nitro group occurs,<sup>7</sup> hence the relative chemical shifts are not comparable with those of the other compounds. Referring to the compounds with only one *ortho* substituent, the <sup>13</sup>C shift to lower and to higher field of derivatives without *ortho* substituents and with two *ortho* substituents, respectively, should be attributed to a lower and higher degree of coplanarity of the methyl group with the phenyl ring, respectively. These results should be compared with those of substituted acetophenones.<sup>12</sup> From previous studies<sup>11</sup> on these compounds it was concluded that the acetyl methyl carbon signal moves downfield on increasing the bulk of *ortho* substituents which move the acetyl group from coplanarity with the phenyl ring. The conformational situation of substituted methyl phenyl sulphoxides can thus be depicted as in the Figure: the conformations reported were drawn according to the calculated <sup>4</sup> geometry of compounds (3c)(a), (1a)(b), and (2a)(c). The twist-angle  $\omega$  of the methyl group is related to that of the SO bond from the phenyl plane by the relationship  $^{13}\omega = \theta + 74.5^\circ$ . According to theory,<sup>4</sup> which qualitatively agrees with a number of experimental determinations,<sup>5,6</sup> one fluorine substituent in an *ortho* position in methyl phenyl sulphoxide causes a decrease of the twist-angle  $\omega$  of the methyl group when compared with the unsubstituted compound and an increase of  $\omega$  when two *ortho* fluorine substituents are present. In both cases the methyl group should reach a position closer to the phenyl ring.

Even for compound (1e) the SO group should be nearly in the plane of the ring since intramolecular hydrogen bonding occurs<sup>14</sup> with the OH group.

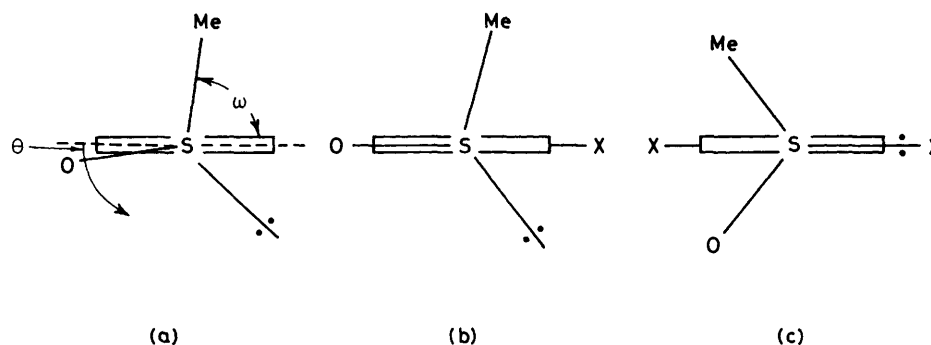
Parallel behaviour is found for <sup>1</sup>H chemical shifts as well, if one excludes compounds (1e) and (1f). The shift is now to increasingly lower field on insertion of one and two substituents in *ortho* positions, as can be seen in Table 3. These shifts to lower field can probably be attributed to the increased contribution from ring currents to the shielding constant of the protons when the methyl group moves toward the plane of the phenyl ring.

\* fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato.

**Table 3.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{17}\text{O}$  Chemical shifts ( $\delta$ -values) relative to the nuclei of the methylsulphinyl group in compounds (1)–(5) and long-range  $^n\text{J}(\text{C}-\text{H})$  coupling constants (Hz) involving the methyl carbon nucleus<sup>a</sup>.

Compound	(1a)	(1b)	(1c)	(1d)	(1e)	(1f)	(2a)	(2b)	(2c)	(3a)	(3b)	(3c)	(4)	(5)
$^{13}\text{C}$	42.19	42.06	41.75	41.33	41.27	43.83	39.95	38.39	38.01	44.07	44.04	43.92	41.53	43.98
$^1\text{H}$	2.80	2.67	2.78	2.74	2.94	2.88	3.06	2.83	3.03	2.64	2.67	2.64	2.81	2.74
$^{17}\text{O}^c$	-10.8	-6.1	-1.1	-10.3	-241.6 <sup>b</sup>	18.0	9.5	6.1	13.6	2.3	2.4	1.1	7.6	3.8
$^4\text{J}(\text{C}-\text{H})$			0.5	0.6 <sub>2</sub>		0.5					0.4	0.4	0.6 <sub>2</sub>	0.5 <sub>4</sub>
$^6\text{J}(\text{C}-\text{H})$			0.5	0.6 <sub>2</sub>		0.5		<i>d</i>	<i>d</i>			0.5		0.5 <sub>4</sub>

<sup>a</sup> These measurements were performed only for the compounds reported. <sup>b</sup> Uncertain assignment: broad band,  $\Delta w_{\frac{1}{2}} \approx 1\,000$  Hz. <sup>c</sup> Reference  $\text{D}_2\text{O}$ , external standard; signal width  $\Delta w_{\frac{1}{2}} = 200\text{--}400$  Hz. <sup>d</sup> Not observed,  $\Delta w_{\frac{1}{2}} = 0.26$  Hz.



**Figure.** Model conformations for: (a) compounds without *ortho* substituents; (b) with one *ortho* substituent; (c) *ortho*-disubstituted compounds. The twist-angle of the methyl group with respect to the phenyl plane is  $\theta + 74.5^\circ$  (see ref. 13).

A number of applications of  $^{17}\text{O}$  chemical shifts to the conformational analysis of sulphoxides have been reported.<sup>15,16</sup> The available data are nevertheless too scanty to allow general conclusions to be drawn. The  $^{17}\text{O}$  n.m.r. shift in sulphoxides appears<sup>15</sup> at higher field than in the corresponding ketones and this, on the assumption that the largest contribution to the shielding constant is given by the paramagnetic term,<sup>15</sup> should depend on lower  $\Delta E$  (average excitation energy) values and on higher multiple-bond character (lower electron density at the oxygen atom) in the CO with respect to the SO bond. The  $^{17}\text{O}$  shifts of diphenyl sulphoxide and phenyl methyl sulphoxide are close,<sup>15</sup> whereas a clear shielding effect is observed<sup>15</sup> in comparison with dimethyl sulphoxide, caused by the phenyl ring. This behaviour is parallel to that observed for ketones,<sup>17</sup> when acetophenone and acetone are compared. Thus, in both cases, it seems that the extent of  $\pi$ -conjugation of the carbonyl and sulphanyl bonds influences the shielding of the oxygen nucleus though to different extents in the two classes of compounds.

The data reported in Table 3 show a number of features. The *para* substituent, in compound (3) and derivatives from literature sources,<sup>15</sup> does not exert an appreciable effect on  $^{17}\text{O}$  n.m.r. shifts. In the *ortho*-substituted derivatives (1a–d), shifts to higher field are observed and they differ for the different *ortho* substituents: they can hardly be understood in terms of electronic effects alone. For compounds (1e) and (1f) the  $^{17}\text{O}$  shielding is affected by direct through-space interactions between the substituent and the SO group: they will thus be omitted from the comparison with other compounds. In derivatives (1a–d) the higher shielding, referred for example to that of compounds (3), should account for the different twist of the SO bond and, more precisely for an increased degree of coplanarity with the phenyl ring. The orientation of the oxygen atom should be *anti* with respect to the *ortho* substituent<sup>6,7</sup> and thus direct through-space interactions with the SO bond will also be minimized.

The  $^{17}\text{O}$  chemical shifts have been widely employed in the

conformational analysis of carbonyl compounds.<sup>17–19</sup> In *ortho*-substituted acetophenones the  $\delta(^{17}\text{O})$  values move downfield on increasing the twist-angle of the carbonyl group and the slope of the correlation<sup>17–19</sup> is  $0.84\text{--}1.16$   $\delta/\text{angle}^\circ$ . This holds, however, when the substituents do not have relevant electronic effects.<sup>19</sup>

In the case of compounds (1), the largest high-field shifts are observed when the substituents are OMe and F, compounds (1a) and (1d). A comparison with the corresponding acetophenones<sup>17</sup> shows that a smaller chemical-shift range is covered by substituted sulphanyl derivatives but a proportionality of the  $^{17}\text{O}$  chemical shifts in the two series of compounds is present. Thus, while one *ortho* substituent in the acetophenones causes deviation of the carbonyl group from the ring plane, in methylsulphanyl derivatives it increases the coplanarity of the SO bond with the phenyl ring as compared with the unsubstituted compound (3c).

As regards compound (4), the further low-field shift with respect to compound (1e) could involve the electron-attracting effect of the *meta* and *para* chlorine substituents.

Derivatives containing two *ortho* substituents, (2), show the  $^{17}\text{O}$  chemical shift at lower field with respect to compounds without *ortho* substituents and at even lower field with respect to those with one *ortho* substituent. According to correlations<sup>17</sup> found between  $\delta(^{17}\text{O})$  and twist-angle in acetophenones, in compounds (2) the SO bond should be less coplanar with the ring plane than in compounds (1) and (3). These facts are in qualitative agreement with the conclusions drawn from LIS measurements, from  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts, and are summarized in the Figure.

**Long-range  $^n\text{J}(\text{C}-\text{H})$  Coupling Constants.**—In coupled  $^{13}\text{C}$  spectra of the compounds investigated herein, long-range coupling constants are observed between carbon and hydrogen nuclei of the ring and the methyl group. Those involving the methyl carbon and ring-hydrogen nuclei have been measured in a number of compounds and appear to show stereochemical

dependence. The  $^{13}\text{C}$  nucleus shows a measurable coupling constant with *ortho* [ $^4J(\text{C}-\text{H})$ ] and *para* [ $^6J(\text{C}-\text{H})$ ] protons. The values extracted from the spectra are reported in Table 3. The stereochemical behaviour of  $^6J(\text{C}-\text{H})$  has been thoroughly investigated in acetophenones,<sup>20</sup> anisoles,<sup>21</sup> and ethylbenzene.<sup>22</sup> For anisole and ethylbenzene, where O and  $\text{CH}_2$  replace the SO group of our compounds, the value of  $^6J(\text{C}-\text{H})$  for a  $90^\circ$  twist of the methyl group from the ring plane amounts<sup>20</sup> to  $(-0.63$  Hz and  $(-0.6_2$  Hz respectively, *i.e.* to very similar values. Furthermore, a  $\sin^2 \theta$  dependence<sup>20</sup> is suggested for rotation of the OMe group. If a similar dependence is assumed for the SOMe group, then for derivatives (1), (3), and (5) the twist of the methyl group from the ring plane should be of the same order of magnitude and included within the range  $70$ – $80^\circ$  (corresponding to an SO deviation of  $\pm 5^\circ$  from the ring plane). According to the same assumption, the  $^6J(\text{C}-\text{H})$  becomes  $< (-0.15$  Hz when the twist-angle of the methyl group is  $< 30^\circ$  (SO deviation from the ring plane  $> 70^\circ$ ).

The  $^4J(\text{C}-\text{H})$  values are almost constant for compounds (1), showing a small influence from electronic effects of the substituent, and range within  $0.5$ – $0.6$  Hz, while the values measured for compounds (3b) and (3c), where no *ortho* substituents are present, seem only slightly lower. In acetophenone and 2-fluoroacetophenone, molecules which are very nearly all-planar, this coupling amounts to  $\pm 0.105$  Hz in the latter<sup>16</sup> and is immeasurably smaller ( $< 0.03$  Hz) in the former.<sup>20</sup>

**Conclusions.**—From the different n.m.r. techniques used for studying the conformational behaviour of methyl phenyl sulphoxides the results obtained, even if only at a qualitative level, show a satisfactory agreement. As regards derivatives (1), the S=O bond is *anti* with respect to *ortho* substituents, nearly coplanar with the phenyl ring, the twist-angle covering the range  $0$ – $30^\circ$ . The distortion is higher in derivatives (2) ( $> 40^\circ$ ), and at an intermediate level in derivatives (3).

The twist-angles obtained from the LIS method appear, in general, to be higher than those predicted from MO *ab initio* calculations<sup>4</sup> but the trend of the effect on the twist-angle on inserting one and two *ortho* substituents is qualitatively the same.

## Experimental

**Compounds.**—Most of the sulphoxides employed in this study are described in the chemical literature. They were obtained by oxidation of the corresponding sulphides with *m*-chloroperbenzoic acid (1 mol equiv.) in  $\text{CHCl}_3$  solution at  $-20^\circ\text{C}$ . Impurities were removed from the crude material by column chromatography [silica gel; ethyl ether–light petroleum (b.p.  $30$ – $50^\circ\text{C}$ ) 1:1 as eluant] followed by distillation under reduced pressure or crystallization. The precursor aryl methyl sulphides were usually obtained by alkylation of arenethiols (commercial or prepared by standard methods<sup>23,24</sup> with methyl iodide under phase-transfer conditions.<sup>25</sup> This procedure was used in particular for the synthesis, as yet unreported, of the following sulphoxides.

**2,6-Dichlorophenyl methyl sulphoxide (2c).** White solid, m.p.  $97$ – $99^\circ\text{C}$  (from cyclohexane) (Found: C, 40.1; H, 2.8; S, 15.7.  $\text{C}_7\text{H}_6\text{Cl}_2\text{OS}$  requires C, 40.2; H, 2.9; S, 15.3%).

**Methyl 2,3,4-trichlorophenyl sulphoxide (4).** White solid, m.p.  $114$ – $116^\circ\text{C}$  (from cyclohexane) (Found: C, 34.8; H, 2.0; S, 12.4.  $\text{C}_7\text{H}_5\text{Cl}_3\text{OS}$  requires C, 34.5; H, 2.1; S, 13.2%).

**3,5-Dichlorophenyl methyl sulphoxide (5).** White solid, m.p.  $71.5$ – $72^\circ\text{C}$  (from hexane) (Found: C, 40.1; H, 2.8; S, 15.7.  $\text{C}_7\text{H}_6\text{Cl}_2\text{OS}$  requires C, 40.2; H, 2.9; S, 15.3%).

**N.M.R. Measurements.**—The spectra were recorded at 200.058 MHz for  $^1\text{H}$ , 50.308 MHz for  $^{13}\text{C}$ , and 27.12 MHz for  $^{17}\text{O}$  on a

Varian XL-200 spectrometer at a probe temperature of  $296$  K. Coupled  $^{13}\text{C}$  spectra (natural abundance) were obtained on  $0.5$ – $0.6$  mol  $\text{dm}^{-3}$  solutions of the compounds in  $[\text{H}^2]\text{chloroform}$ . No attempts were carried out to determine the relative sign of  $^nJ(\text{C}-\text{H})$  coupling constants. For compounds (1b) and (2b) weak irradiation of the protons of the methyl groups bonded to the ring was necessary in order to eliminate long-range couplings with these protons. A spectral width of  $1000$ – $1500$  Hz was adopted with 32K data points,  $30$ – $45^\circ$  pulse angle, and  $2000$ – $5000$  scans. For  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts SiMe<sub>4</sub> was employed as internal standard.

The  $^{17}\text{O}$  spectra (natural abundance) were recorded without sample spinning and with the lock on. The reference was external  $\text{D}_2\text{O}$  in a coaxial tube. The sample solutions were the same as employed for  $^{13}\text{C}$  measurements. The instrumental settings were: spectral width 30 kHz, acquisition time 20 ms,  $90^\circ$  pulse angle,  $2 \times 10^5$  to  $1 \times 10^6$  scans. A three-pulse sequence was employed,<sup>26</sup> in order to minimize the acoustic ringing, of the type:

$$D_1 - 90_x - D_3 - \text{FID}^+$$

$$D_1 - 180_x - \tau - 90_x - D_3 - \text{FID}^+$$

where  $D_1 = 50$  ms,  $\tau = 80$   $\mu\text{s}$  and  $D_3 = 40$   $\mu\text{s}$ . The data-point resolution was improved to 0.3 p.p.m. by zero-filling to 8K data points. The signal-to-noise ratio was enhanced by applying a 30 Hz exponential broadening factor to the FID prior to Fourier transformation. The reproducibility of the chemical shift was estimated to be  $\pm 1.0$  p.p.m.

The reagent shift employed for LIS measurements on  $^1\text{H}$  and  $^{13}\text{C}$  was Yb(fod)<sub>3</sub> dried *in vacuo* over phosphorus pentoxide, added in known and increasing amounts to  $[\text{H}^2]\text{chloroform}$  solutions (0.3 mol  $\text{dm}^{-3}$ ) of the substrate examined. The maximum molar ratio between Yb(fod)<sub>3</sub> and the substrate was 0.1. The correlation coefficients for the plots relating chemical shifts to the lanthanide:substrate ratio were always found to be  $\geq 0.999$  and the intercepts were identical with the unshifted spectral data.

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## References

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