# Stereodynamical Processes in β-Substituted Symmetric Isopropyl Radicals

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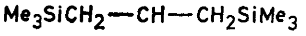
Addition of trimethylsilyl ($\mathrm{Me_3Si\cdot}$) and methylthiyl ($\mathrm{MeS\cdot}$) radical to $\mathrm{Me_3SiCH_2{-}CH{=}CH_2}$ and $\mathrm{MeSCH_2{-}CH{=}CH_2}$ yields, respectively, the radicals $\mathrm{Me_3SiCH_2\dot{C}HCH_2SiMe_3}$ (I) and $\mathrm{MeSCH_2\dot{C}HCH_2SMe}$ (II) which were observed by e.s.r. spectroscopy. Restricted rotation about the $\mathrm{\cdot CH{-}CH_2}$ bonds was detected below −100 °C † and the free energy of activation determined [3.4 for (I) and $2.8_5$ kcal ‡ $\mathrm{mol^{-1}}$ for (II), respectively]. The features of the line shapes also showed that the conformation of (I) is symmetric whereas that of (II) is asymmetric. The geometry of these conformations was also assessed and the angle $\phi$ between the $2p_z$ orbital of $\mathrm{\cdot CH}$ and the C–X bond was found to be 4—5° § when X = $\mathrm{SiMe_3}$ (I) and 10—11° when X = MeS (II). The dependence of the β-splitting on the conformation and on the electronic properties of silicon and sulphur was studied by INDO calculations and the hypothesis that sulphur-containing radicals must be distorted to account for their low $a_{\mathrm{H}\beta}$ splitting is challenged.

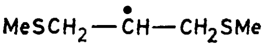
Addition of trimethylsilyl ($\mathrm{Me_3Si\cdot}$) and thiyl ($\mathrm{MeS\cdot}$) radicals to double bonds generates carbon-centred radicals which can be observed by e.s.r. spectroscopy in appropriate steady-state conditions.[1] This technique allows the conformational arrangements of a variety of free radicals to be elucidated. For instance the conformations of simple radicals obtained by addition of $\mathrm{R_3Si\cdot}$ and $\mathrm{RS\cdot}$ to ethylene and other alkenes have been investigated.[2-5]

These kinds of radicals are also suited for the study of motions connected with rotational processes; [2,3] this fact prompted us to investigate the symmetric radicals (I) and (II) generated by addition of $\mathrm{Me_3Si\cdot}$ and $\mathrm{MeS\cdot}$ to $\mathrm{Me_3SiCH_2CH{=}CH_2}$ and $\mathrm{MeSCH_2CH{=}CH_2}$, respectively. In principle, we expected that in these radicals rotation about the $\mathrm{CH_2{-}\dot{C}H}$ bond on one side of the radical may occur either in a conrotatory or disrotatory manner with respect to the other symmetric side. The purpose of the present work was to ascertain which rotation pathway is preferred, as well as to determine the corresponding activation energy; in addition conformational preferences were assessed by a combination of experimental evidence and theoretical calculations.



$\mathrm{Me_3SiCH_2{-}CH{-}CH_2SiMe_3}$

(I)

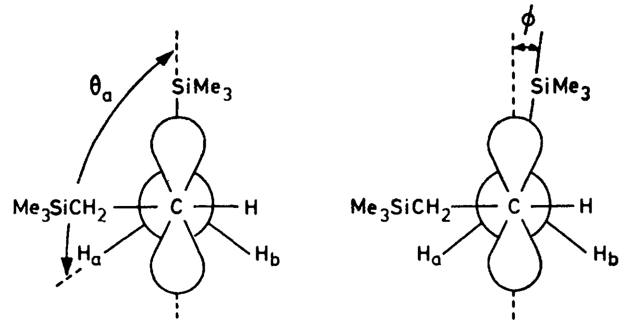


$\mathrm{MeSCH_2{-}\dot{C}H{-}CH_2SMe}$

(II)

## RESULTS AND DISCUSSION

*E.s.r. Spectra.*—The e.s.r. spectrum of radical (I) displays, at −40 °C, two hyperfine splitting constants, $a_{\mathrm{CH}}$ −20.1 (almost temperature independent) and $a_{\mathrm{CH}_2}$ 17.1 G (temperature dependent). ¶ The negative and positive signs have been assigned on the basis of INDO calculations. The 17.1 G splitting corresponds to four equivalent hydrogens (two equivalent methylene groups) at −40 °C, whereas at −150 °C two splittings are observed, each corresponding to a pair of hydrogens, $a_{\mathrm{H}}$ $19.2_5$ and $12.2_5$ G. The large difference between these two values requires the existence of a conformation in which the two β-CH bonds of the $\mathrm{CH_2}$ group have different angles θ with respect to the direction of the $2p_z$ orbital bearing the unpaired electron. An eclipsed conformation, (*i.e.* a conformation having a zero value for the angle $\phi$ between the C–Si bond and the direction of the $p$-orbital) would not explain the experimental $\Delta a_{\mathrm{H}}$ of 7 G. The difference between the two hydrogens ($\mathrm{H_a}$ and $\mathrm{H_b}$) within a methylene group should be due only to the spatial environment which cannot cause such a large difference (Scheme 1).



Scheme 1

In order to estimate the deviation from the eclipsed arrangement, the value of $\theta_a$ defined as in Scheme 1 (and consequently of $\theta_b = \theta_a + 120$ and $\phi = 120 - \theta_a$) can be assessed by making use of the equation (1) where $i$ is either a or b.

Since $A$ is known to be small,[6,7] with a probable value of 2 G,[8-10] it is convenient to assume this value for $A$ and search for values of $B$ and $\theta_i$ best fitting equation (1). This can be done in the present case in that two β-splittings have been measured and thus two equations can be set up for estimating the two unknowns. In the

$$a^i_{\mathrm{H}\beta} = A + B\cos^2\theta_i \qquad (1)$$

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† °C = K − 273.15.
‡ 1 cal = 4.184 J.
§ 1° = (π/180) rad.
¶ 1 G = $10^{-4}$ T.

case of (I) we obtain $B$ 54.3 G and $\phi$ 4.3° thus indicating that a small deviation from the conformation where the C–Si bond eclipses the $p_z$ orbital is sufficient to account for the difference of the $a_{H\beta}$ values.

The e.s.r. spectrum at −20 °C of $MeSCH_2\dot{C}HCH_2SMe$ (II) has a methine splitting ($a_{CH}$ −21.2$_5$ G) that is not temperature dependent and a methylene splitting ($a_{CH_2}$ 14.75 G, due to four equivalent hydrogens) whose value does depend on the temperature. On lowering the temperature, a selective broadening of some lines occurs, as in the case of (I), and at −150 °C two different values for the methylene splittings are observed, each corresponding to a pair of hydrogens (Table 1). By applying the same approach as for (I) we obtain $B$ 39.3 G. and $\phi$ 11.4°: the deviation from the eclipsed conformation seems to be larger. Also, the $B$ value is smaller than in (I) with a difference which exceeds what is considered the 'normal' range [8,9] of $B$ (48 ± 5). Krusic and Kochi suggested [2] that in this kind of sulphur-containing radical the CS bond is tilted with respect to the direction of the $p_z$ orbital of the trigonal carbon, so that equation (1) is not applicable. In the theoretical section the whole problem of the validity and applicability of equation (1) is reinvestigated.

TABLE 1

Hyperfine splitting constants (G) for radicals $XCH_2{-}\dot{C}H{-}CH_2X$, X = $Me_3Si$ (I) and X = MeS (II). The values of $B$ and $\phi$ obtained by equation (1) with $A$ assumed equal to 2 G are also given (see text). The free activation energy to the $CH_2{-}\dot{C}H$ rotation is in kcal mol$^{-1}$

| Radical | Temperature (°C) | $a_{CH}$/G | $\bar{a}_{2CH_2}$/G | $a_{CH_2}$/G | $a_{CH_2}$/G | $B$/G | $\phi$ (°) | $\Delta G^{\ddagger}$ |
|---|---|---|---|---|---|---|---|---|
| (I) | −40 | −20.1 | 17.1 | | | | | |
| | −150 | −19.8 | | 12.2$_5$ | 19.2$_5$ | 54.5 | 4.3 | $3.4 \pm 0.1_5$ |
| (II) | −20 | −21.2$_5$ | 14.75 | | | | | |
| | −150 | −21.2$_5$ | | 6.0 | 19.2$_5$ | 39.3 | 11.4 | $2.8_5 \pm 0.1_5$ |

The fact that both radicals do show line broadening indicates that a dynamic process occurs, most likely restricted rotation about the $CH_2$–CH bond. In the case of radical (I) the dependence of the linewidth on temperature could be reproduced by means of a computer program [11] which takes into account the exchange of the two splittings observed at low temperature. From the first-order rate constants, obtained by fitting the experimental to the computed spectra (Figure 1), an average value of the free energy of activation ($\Delta G^{\ddagger}$ 3.4 ± 0.1$_5$ kcal mol$^{-1}$) was obtained. Although apparently similar to the behaviour of (I) an important difference is observed in the line broadening of (II). In (I) the ratio of the heights between the first line (never broadened by exchange) and the fourth line (broadened by exchange) varies from the initial 1 : 6 value of the fast exchange region (*ca.* −30 °C) to the expected 1 : 4 ratio of the intermediate exchange region. The intermediate exchange region corresponds to the temperature range where the second line, due to the averaging of the two non-equivalent $CH_2$ splittings, becomes so broad as to be undetectable (coalescence).[12-15] In the case of (II), on the other hand, when the second line disappears, having reached the coalescence point, the ratio between the first and fourth line is 1 : 3 rather than 1 : 4 in disagreement with our expectations and with the behaviour of (I). Consequently spectral simulation could not be achieved using the two methylene splittings measured at low temperature.

This apparent discrepancy can be explained if the conformation of (II) is assumed to have lower symmetry than that of (I); in this conformation the two hydrogens with the large β-splittings, as well as those with the small one, are expected not to be identical, as in (I). The internal difference, however, is quite small and, at the low temperatures required to detect the rotational process, is of the same order of magnitude as that of the viscosity broadened linewidth. As a consequence one cannot observe a further splitting for the β-hydrogens of (II), but only lines broader than in (I). This broadening only occurs to the lines affected by the non-equivalence of the pair of β-hydrogens and not to those unaffected as, for instance, the first line. Actually, as the viscosity effects are equal in radicals (I) and (II) at the same temperature, this line has the same width in both radicals. The ratio between the heights of the first and fourth line must then be larger in (II) with respect to (I) ($\frac{1}{3}$ against $\frac{1}{4}$). According to this interpretation, if the large β-splitting (19.2$_5$ G for both hydrogens) is substituted by a pair of values differing by 0.7 G (*i.e.* 1H 19.6 and 18.9 G) the lineshape can be correctly simulated (Figure 2) and $\Delta G^{\ddagger}$ 2.8$_5$ ± 0.15 kcal mol$^{-1}$ obtained. Such a small difference in the β-splittings cannot obviously be due to different values of the angles θ (where θ is the dihedral angle between the β-CH bond and the direction of the $p_z$ orbital bearing the unpaired electron) but to the difference in the chemical environment experienced by the pair of β-hydrogens. It is also conceivable that this difference is detectable only in the case of a large splitting, whereas it is probably negligible for a smaller splitting such as the 6.0 G of the second pair of β-hydrogens; accordingly no attempt was made to guess this difference since it did not affect the line shape simulation. To support the hypothesis that the conformer of (II) has a symmetry lower than that of (I) we propose an arrangement where the angle θ is the same for the two β-hydrogens within each pair but the chemical environment is different. Such a conformation can actually exist (see for instance conformation G in Figure 3) and when we calculate, with the INDO approximation, the splittings expected for the case $\phi$ 11° (*i.e.* for the conformation experimentally derived *via* the $A + B\cos^2\theta$ relationship)

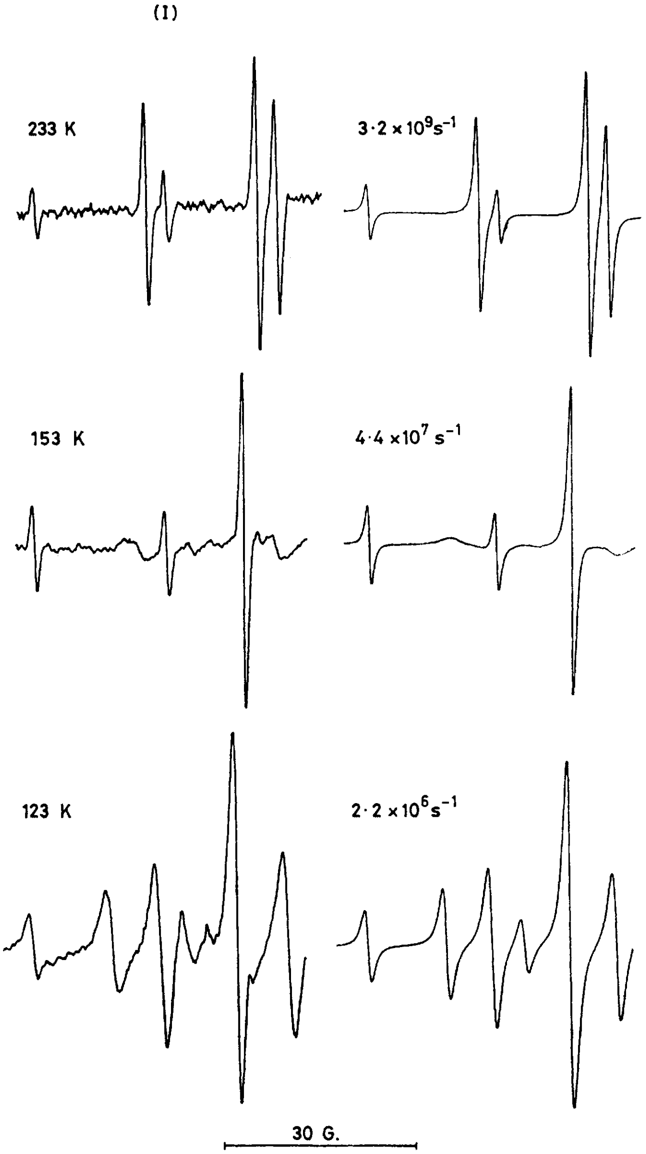


FIGURE 1 Experimental half-e.s.r. spectrum (downfield part) of $Me_3Si{-}CH_2{-}\dot{C}H{-}CH_2{-}SiMe_3$ (I) at three selected temperatures (left) and computed patterns (right) obtained with the kinetic constants reported. The resulting $\Delta G^\ddagger$ is $3.4 \pm 0.15$ kcal mol$^{-1}$

we obtain 19.2 and 18.2 G, in good agreement with the values (19.6 and 18.9 G) used to match the experimental line shape. The same INDO calculations also predict, for the other pair of β-hydrogens, splittings of 5.1 and 5.6 G; as anticipated this difference seems smaller than the other.

In order to understand better the different dynamic behaviour of (I) and (II) we have also to take into account in more detail the possible conformations involved in the rotational process of the two radicals. Let us first decide whether the conformations are of the type *syn* or *anti* (Scheme 2), *i.e.* whether the substituents $SiMe_3$ and SMe are on the same or on the opposite side, respectively, of the $CH_2\dot{C}HCH_2$ plane.

It is convenient to discuss the two radicals separately beginning with $Me_3SiCH_2\dot{C}HCH_2SiMe_3$ (I). Simple inspection of molecular models indicates that the *syn*-conformation of (I) is ' forbidden ' in that the methyl groups are much closer than the sum of their van der Waals radii. Accordingly, when the energies are estimated by means of INDO calculations, that of *syn* is predicted to be 177 kcal mol$^{-1}$ higher than *anti*, even for the situation with the minimum interaction between the methyl groups. Despite the approximations involved in the INDO approach such an extraordinary difference is a good indication that the *syn*-conformer is so sterically crowded as to be forbidden not only as a fundamental state, but also as a transition state of the rotation pathway. Little doubt is thus left that the conformation of (I) is *anti*. The low temperature e.s.r. spectrum also indicates that the conformation of (I) has $C_2$ symmetry since there are two pairs of equivalent β-hydrogens. There are

FIGURE 2 Experimental half-e.s.r. spectrum (downfield part) of $MeS{-}CH_2{-}\dot{C}H{-}CH_2{-}SMe$ (II) at three selected temperatures (left) and computed patterns (right) obtained with the kinetic constants reported. The resulting $\Delta G^\ddagger$ is $2.85 \pm 0.15$ kcal mol$^{-1}$

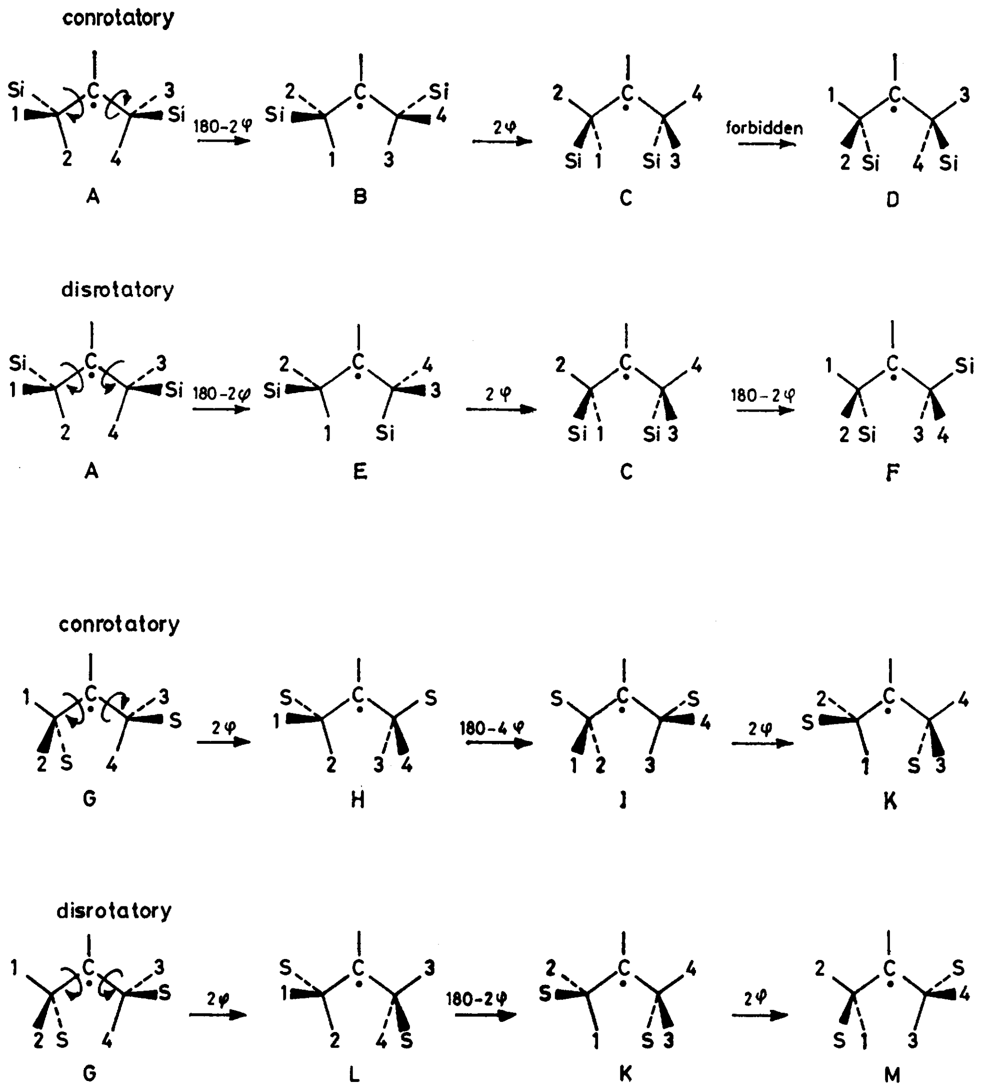


**Figure 3** Conformational isomers of radicals (I) and (II) according to the conrotatory and disrotatory rotation pathway

two different *anti*-conformations that fulfill this requirement: both have a two-fold symmetry axis coincident with the CH bond of the methine carbon (point group $C_2$). These conformers are labelled A and C in Figure 3: they have been drawn with $\phi$ 30 rather than 4° since in this way they can be better represented in two dimensions. Conformers A and C are different in that one is more crowded than the other and are thus expected to have very different splittings for their β-hydrogens: $a_{H\beta}$ is strongly dependent on $\phi$ and the two conformers mentioned should have different $\phi$ values, hence different $a_{H\beta}$ splittings, owing to their different steric requirements. Since at −150 °C, when the motion is slow on the e.s.r. time scale, only one symmetric conformer is observed experimentally, it should be either A or C and not a mixture of the two. This fact also rules out the possibility that line broadening is due to an exchange between two different conformers. The e.s.r. spectrum also shows that the hydrogens with the larger coupling ($19.2_5$ G) exchange with those with the smaller ($12.2_5$ G): in Figure 3 (conformer A) we labelled the former 1,3 and the latter 2,4. The motion has therefore to fulfill this requirement also, in addition to the previously mentioned restrictions. As a whole the motion must obey the following conditions: (i) the exchange occurs between hydrogens belonging to chemically equal conformers (topomers or enantiomers); (ii) the conformers must have $C_2$ symmetry; (iii) in the rotation pathway the *syn*-conformers are not allowed, not even as transition states; (iv) hydrogen 1 exchanges with 2, and 3 with 4 (Figure 3).

**Scheme 2**

There are two types of possible motions: conrotatory and disrotatory (Figure 3). Let us first analyse the conrotatory motion. Conformer A has the required $C_2$ symmetry and can exchange correctly its β-hydrogens yielding the enantiomer B with a conrotatory 180–2 $\phi$ rotation; in this process all four restrictions are obeyed. Another conformer (labelled C) has the required $C_2$ symmetry and with a conrotatory 180–2 $\phi$ rotation can exchange its β-hydrogens yielding the enantiomer D, but to do so must go through the 'forbidden' *syn* arrangement. Conformer A can also yield conformer E with disrotatory rotation (Figure 3): however whereas the exchange of 1 with 2 agrees with the experiment the exchange of 3 with 4 does not, since in E both 3 and 4 correspond to larger couplings (*i.e.* their $\theta$ angles are equal and small), In other words E has lost the required $C_2$ symmetry; the same result is obtained for the disrotatory motion of C to give F. The only way of carrying out a motion between two equivalent $C_2$ conformers in a disrotatory manner is a 360° rotation of A or C, to reproduce themselves. But obviously in this case there is no spin exchange whatsoever. Finally, exchange of A with C either in a conrotatory or a disrotatory manner violates the first condition.

As a result only conformer A exchanging with B in a conrotatory manner fulfills all the mentioned restrictions.

Similar analysis can be carried out to explain the different e.s.r. features observed for $MeSCH_2\dot{C}HCH_2SMe$ (II). Again we have to decide which is the basic conformation (*anti* or *syn*); the choice now is not so obvious as in the case of (I), although inspection of molecular models seems to indicate that *anti* is less hindered than *syn*. We thus tried to obtain some indication from INDO calculations; they predict that even in the most favourable conditions (*i.e.* with the two *syn*-methyls pointing in opposite directions) the *syn*-conformer is still 4 kcal $mol^{-1}$ less stable than the *anti*-conformer. This situation is, however, unrealistic since the C–S rotation will certainly bring the two methyl groups closer to each other. When even the most favourable rotation is considered (*i.e.* a correlated torsional motion of the C–S bond which always avoids the overlapping of the two methyls) the energy gap between *syn* and *anti* is predicted to increase to 7 kcal $mol^{-1}$ but with a rotational barrier of 50 kcal $mol^{-1}$, in obvious disagreement with experiment. Although these figures must be regarded with caution,[16,17] their order of magnitude seems to suggest that the fundamental state of radical (II) is *anti* rather than *syn*. However, owing to the much lower energy difference than for radical (I), we cannot rule out that radical (II) assumes the *syn*-arrangement as a transition state for its rotational pathway: accordingly, we feel that restriction (iii) should be lifted in the case of (II). Also, since in the experimental spectrum the two large β-splittings were found not to be identical, the symmetry becomes $C_s$ rather than $C_2$, thus modifying condition (ii). Restrictions (i) and (iv), on the other hand, still hold in that only one kind of radical has been detected for (II), as for (I), and the spin exchange occurs again between the larger and smaller splittings.

In Figure 3 one can see that conformer G has two large and two small splittings as well as the required $C_s$ symmetry; for, the pair of hydrogens 2 and 3 have equal $\theta$ angles even though they have different chemical environments. The same applies to the pair of hydrogens 1 and 4. If conrotatory motion is assumed only the enantiomer K has the required $C_s$ symmetry: conformers such as H and J have, in fact, three large and one small splittings, in contrast with the experimental findings. However an equilibrium between G and K does not allow spin exchange between large and small splittings, thus violating restriction (iv). Under these circumstances the motion of (II) cannot be conrotatory. On the other hand, if a disrotatory motion is considered (Figure 3d) conformer G might interconvert with L and still obey all the mentioned conditions. Furthermore the G–L exchange (corresponding to a 2 $\phi$ disrotatory rotation) is not the only possible exchange; also the 180–2 $\phi$ rotation of L to give K fulfils all the conditions. The only difference between these two situations is that G and L are topomers whereas L and K are enantiomers but e.s.r. cannot distinguish between the two cases. In other words the disrotatory motion can correctly exchange the β-hydrogens of I either *via* a 2 $\phi$ rotation (G to L) or *via* a 180° rotation (G to L and L to K). In the latter event K can also interconvert with M and, eventually, conformer G can be reproduced after a 360° disrotatory rotation. There is no way of distinguishing between a 'short' (2 $\phi$) or a 'complete' (360°) rotation but this is immaterial for our purposes. We may thus conclude that, given an *anti*-conformation as for (I), the motion of (II) is opposite, *i.e.* disrotatory rather than conrotatory. On the other hand if the conformational predictions of the INDO approach are not trusted and radical (II) is assumed to be *syn*, the same kind of analysis leads to the conclusion that the motion is conrotatory. This means that either (I) and (II) have opposite conformation but equal (conrotatory) motion or have the same conformation (*anti*) but opposite motion. The latter situation seems more likely.

We have now to discuss the possibility that the identity of the β-splittings for each pair of hydrogens in (I) be due to an accidental coincidence. If so, (I), like (II), would have $C_s$ symmetry. We observed that the spectral shape of (I) can still be matched by computer simulation if the large β-splitting ($19.2_5$ G) is assumed to be due to a pair of values differing by 0.2 G (*i.e.* $19.1_5$ and $19.3_5$ G). Owing to the viscosity at these low temperatures we cannot have better resolution. We thus tried, by using INDO calculations, to obtain some indication whether the chemical environment, in the case of (I), is expected to have a smaller effect on the β-splittings with respect to (II).

The computation predicts, for radical (I) in the $C_s$ conformation ($\phi$ 5°), a greater difference of the large β-splittings with respect to that of radical (II) in its $C_s$ conformation ($\phi$ 11°). The computed values for (I) are 19.8 and 21.7 G, to be compared with those computed for (II) (18.2 and 19.3 G), or with those observed for (II) (18.9 and 19.6 G). According to these calculations, if (I) had $C_s$ symmetry the difference of the β-splittings would be larger ($\Delta a_{H\beta}$ 1.9 G) and not smaller than that of (II) (computed $\Delta a_{H\beta}$ 1.1 G, observed $\Delta a_{H\beta}$ 0.7 G). The hypothesis under discussion requires a much smaller difference in (I) ($\Delta a_{H\beta} \leqslant 0.2$ G) than in (II). The calculations seem therefore to support the existence of real, rather than accidental, $C_2$ symmetry in (I). In addition the INDO approximation also predicts that conformer A of radical (I), with $C_2$ symmetry, has an energy lower by 1.3 kcal mol$^{-1}$ with respect to the corresponding situation with $C_s$ symmetry as well as by 2.7 kcal mol$^{-1}$ with respect to the other conformer C having $C_2$ symmetry ($\phi$ being obviously taken equal to 5° in all these conformers).

Although this model seems to explain all the details of the different behaviour of (II) relative to (I) and agrees with the experimental observations as well as with the theoretical suggestions of INDO calculations, there are other possibilities worth discussion. Two, in particular, deserve some attention.

(1) An apparently similar linewidth effect was observed [18] in the radical $\cdot CH_2CH_2F$; the authors suggested that this radical exists in two rotational conformers differing by a 90 ° torsional angle. We think that such a model does not apply in the present case for the following reasons. In ref. 18 the motion could not be locked and the two conformers escaped direct observation: therefore the hypothesis of two conformers cannot be eliminated in the case of $\cdot CH_2CH_2F$. In our case the motion was locked, but two such conformers were not observed: if present they should certainly have been noticed since their $a_{H\beta}$ (and also $a_{H\alpha}$) splittings must be very different [see restriction (i)]. In addition the average $a_{H\beta}$ of $\cdot CH_2CH_2F$ is quite large [18] ($27.3_5$ G) and can reasonably be explained with the averaging of the $a_{H\beta}$ splittings of two such conformers, whereas in our case the average value of (II) is too small ($14.7_5$ G) to agree with such an hypothesis.

(2) A second possibility to account for the line shape of (II) is that, in addition to the $CH_2-\dot{C}H$ rotation, a second motion is also restricted at low temperature. This second motion is required, however, not to occur (or be detected) in (I). Restricted $CH_3S-CH_2$ rotation could, in principle, satisfy such a requirement. However, if the model for conformer G (Figure 3) accompanied by a disrotatory motion is rejected and radical (II) is assumed to have the same conformation A (Figure 3) as (I) then, to account for the observed $C_s$ symmetry, one SMe should be locked in a position different from that of its companion. In other words, assuming restricted C–S rotation, radical (II) should have a conformation like that in Scheme 3a rather than Scheme 3b.

a b

SCHEME 3

This model would satisfy the experimental e.s.r. spectrum of (II), although it is not clear why one SMe should prefer an arrangement different from that of its companion. Also, it does not look very likely that the more hindered conformer in Scheme 3a would be preferred to that in Scheme 3b where the two SMe groups experience smaller and symmetric steric effects. The model of Figure 3 seems therefore more conceivable although one cannot, in principle, exclude the hypothesis of Scheme 3.

b *Calculations*.—The experimental hyperfine splitting constants of (I) and (II) confirm that $\langle \bar{a}_{H\beta} \rangle$ values in sulphur-containing radicals are smaller than in the corresponding silicon-containing radicals (14.75 *versus* 17.1 G at *ca.* −30 °C) as reported for a number of similar cases.[2,3,8] To explain this finding Krusic and Kochi suggested [2] that the β-hydrogens in sulphur-containing radicals are tilted with respect to their tetrahedral positions. To support such an hypothesis they carried out INDO calculations using, as a model for $\cdot CH_2CH_2SR$, the ethyl radical since at that time they had not the facilities to test the theory on a sulphur-containing radical itself. They observed that the experimental temperature dependence of $a_{H\beta}$ in $\cdot CH_2CH_2SCH_3$ could not be reproduced by calculations carried out on $\cdot CH_2-CH_3$ with standard geometry, whereas agreement was obtained if the methyl hydrogens were tilted by 15° toward the radical centre.[2] We thus made INDO calculations on $\cdot CH_2CH_2X$ (X = H, SMe, or $SiMe_3$) and found that the β-splittings do depend on the nature of X; the ethyl radical therefore is not a correct model for $\cdot CH_2CH_2SMe$. In addition, whereas equation (1) correctly describes the angular dependence of the β-splitting when the three substituent are equal (as in the case of the three hydrogens in the ethyl radical) it is not adequate, in principle, when X is different from hydrogen. The $B$ term represents the direct electronic transfer between the radical centre and the β-protons in either direction (hyperconjugation) and was found to depend upon the energy difference [19] between the singly occupied MO (SOMO) of the radical fragment ($\cdot CH_2$ in the present case) and the doubly occupied (or vacant) MO of appropriate symmetry of the substituent in the β-position (here $-CH_2-X$). The coefficients of the atomic orbitals and the energy of the latter MO vary with the position assumed by the X group with respect to the trigonal axis of the radical centre and therefore a third empirical constant has to be employed to account for the changes of conjugation due to these changes of symmetry. Geometric requirements indicate equation (2) to be most suitable where $i$ = a or b

$$a_{H\beta}{}^{i} = A' + B'\cos^2[\theta_a + 120°(1 - \delta_{ai})] + C'\sin 2(\theta_a - 75) \quad (2)$$

and $\delta_{ai} = 1,0$ for $i$ = a or b.

In order to test the validity of equation (2) and to determine the influence of X upon the $B$ term of equation (1), INDO calculations on $\cdot CH_2CH_2X$ (X = H, $SiMe_3$, or

SMe) were carried out using, for the third row elements, the parametrization of Benson and Hudson[20] which gave good results on other sulphur- and silicon-containing radicals.[19-21] Standard angles and bond lengths where used: for the $C_\alpha$–$C_\beta$ bond the value 1.55 Å was employed in that it reproduces perfectly the experimental $a_{H\beta}$ value of the ethyl radical (26.8 G).

The value of the C–C length used in ref. 2 not only is unreasonably long but gives a β-splitting (23.2 G) in poorer agreement with the experimental value of the ethyl radical. The value quoted (1.58 Å) in ref. 2 is probably a misprint.

TABLE 2

Coefficients of equations (1) and (2) (see text) best fitting the INDO-computed $a_{H\beta}$ values as a function of the C–C rotational angle $\phi$. The $a_{H\beta}$ values obtained from INDO calculations for the eclipsed conformation ($\phi$ 0°) are also given

| | $a_{H\beta}$/G ($\phi$ 0°) | Equation (1) | | Equation (2) | | |
|---|---|---|---|---|---|---|
| Radical | INDO | *A* | *B* | *A′* | *B′* | *C′* |
| $Me_3SiCH_2\dot{C}HCH_2SiMe_3$ (I) | 16.7 [a] | 2.0 | 47.3 | 0.0 | 51.9 | 3.7 |
| $\cdot CH_2CH_2SiMe_3$ | 19.2 | 2.2 | 54.0 | 0.0 | 57.9 | 4.4 |
| $\cdot CH_2CH_3$ | 14.2 | 1.7 | 50.1 | 1.7 | 50.1 | 0.0 |
| $\cdot CH_2CH_2SMe$ | 11.5 | 1.8 | 47.6 | 3.3 | 44.4 | −3.0 |
| $MeSCH_2\dot{C}HCH_2SMe$ (II) | 11.2 [a] | 1.3 | 44.1 | 2.8 | 41.5 | −1.9 |

[a] Averaged value.

The conclusions, derived from our calculations on $\cdot CH_2CH_2X$ (X = H, SMe, or $SiMe_3$) can be summarized as follows.

(a) The INDO-computed hyperfine splitting constants are better reproduced by equation (2) than (1), as expected since an additional parameter has been added. As one can see in Table 2 the maximum deviation between the two equations occurs for X = $Me_3Si$, where $C'$ has a maximum whereas $C' = 0$ for X = H as expected.

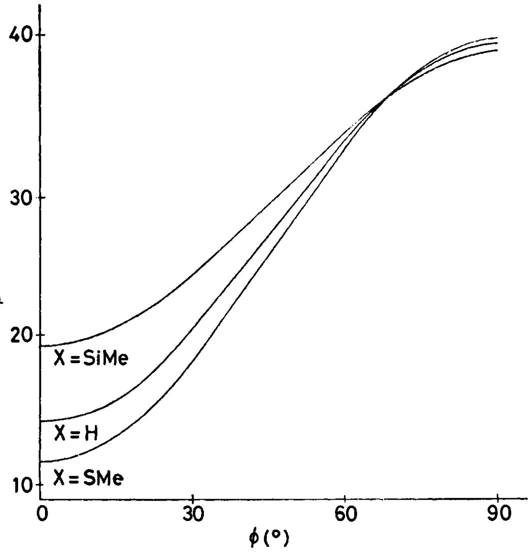
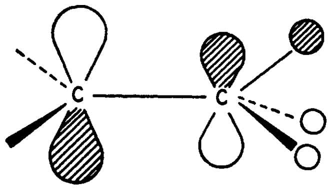


FIGURE 4 Dependence on the rotational angle $\phi$ (see text) of the INDO-computed $a_H$ mean values of the β-hydrogens in the radicals $\cdot CH_2CH_2X$ (X = H, $SiMe_3$, or SMe). In the eclipsed conformation ($\phi$ 0°) the largest difference among $\bar{a}_{H\beta}$ is observed, whereas in the range $\phi$ 65—70° the three values become coincident. It is also evident that for any $\phi$ smaller than 15°, electronic effects make $\bar{a}_{H\beta}$ of $\cdot CH_2CH_2SMe$ lower than the approximate low temperature limit for a primary alkyl radical (13.5 G) established in reference 2

(b) The mean values of the computed $a_{H\beta}$ splittings appear to depend significantly on the nature of X (Figure 4), particularly in the region where C–X eclipses the $2p_z$ carbon orbital (*i.e.* for $\phi$ 0°). In fact the phase of the atomic orbital of the SOMO in $\cdot CH_2CH_3$ shows that the main interaction is that between the SOMO of $\cdot CH_2$ and the doubly occupied pseudo-π-molecular orbital of the $CH_2X$ moiety (Scheme 4). This agrees with the general observation that $\Delta E_{(SOMO-\pi CH_2X)}$ is much smaller than $\Delta E_{(SOMO-\pi^* CH_2X)}$; as a consequence $\bar{a}_{H\beta}$ is proportional to the reciprocal of the energy gap between the SOMO of $\cdot CH_2$ and the pseudo-π-MO of $CH_2X$.[22]



SCHEME 4

Actually, the energy levels computed for $\cdot CH_2$ and $\cdot CH_2X$ fragments show that the energy gaps corresponding to $CH_2SMe$, $CH_3$, and $CH_2SiMe_3$ follow the opposite trend of the β-splittings ($SiMe_3 \gg H > SMe$). It is also worth mentioning that the spin density of the β-protons for X = SR can be further decreased with respect to the ethyl radical, by the direct mixing of the SOMO of $\cdot CH_2$ with the sulphur lone pair ($n_S$).

(c) When the substituent is coplanar with the $\cdot CH_2$ plane ($\phi$ 90°) the $\bar{a}_{H\beta}$ are nearly independent of the electronic nature of X (Figure 4). This indicates a very small inductive effect, as already pointed out by Krusic and Kochi.[2]

(d) When the Boltzmann distribution over all the rotational states is taken into account, our calculations match the experimental temperature dependence[2] of the $\cdot CH_2CH_2SMe$ β-splitting even better than reported in ref. 2, without introducing any distortion. The C–C rotational barrier best reproducing such a dependence is 2.0 kcal $mol^{-1}$ (Figure 5), a value close to that we experimentally found ($2.8_5$ kcal $mol^{-1}$) for the analogous radical (II). To verify independently the latter conclusion an *ab initio* calculation at the STO 4-31G level (more reliable than the INDO approximation) was carried out on

$\cdot CH_2CH_2SX$ (X = H rather than Me for reasons of economy). The SCC angle was allowed to vary and the minimum energy structure was found to correspond to an SCC angle of 112.4°, a value that only differs by 3° from the standard 109° and is thus far from that (109 − 15° = 94°) proposed in ref. 2. The *ab initio* calculations also predict a rotational barrier about the $\cdot CH_2$–$CH_2SH$ bond of 1.7 kcal $mol^{-1}$, a value almost identical to that (2.0 kcal $mol^{-1}$) predicted by fitting, with INDO calculations, the temperature dependence of the β-splittings of $\cdot CH_2CH_2SMe$ (see Figure 5).

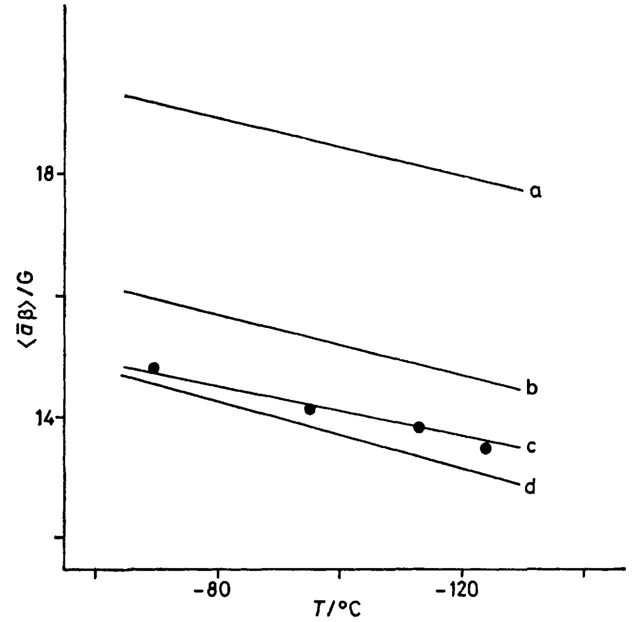


FIGURE 5 Experimental dependence (full circles) of the $\bar{a}_{H\beta}$ splitting of $\cdot CH_2CH_2SMe$ on temperature as taken from ref. 2. Lines a and d are those calculated in ref. 2 with standard (line a) and distorted (line d) geometry, assuming a CC rotational barrier of 1.5 kcal $mol^{-1}$. Lines b and c are those calculated in the present work with standard geometry and with a rotational barrier of 1.5 and 2.0 kcal $mol^{-1}$ respectively. Line c thus represents the best agreement between theory and experiment (see text)

According to these considerations the smaller values of the β-splittings in sulphur-containing radicals with respect to silicon or other substituted radicals, should not be due to distorted geometry but to the electronic effects mentioned before, *i.e.* a reduction of the electron-releasing power from the CH bond of the $CH_2X$ group toward the radical centre, as already suggested by Symons *et al.*[23,24]

We also point out that the simple equation (1), although not exact, is still adequate to assess the conformation of the sulphur-containing radicals from the experimental $a_{H\beta}$ splittings, since the $C'$ term is small. For radical (II), in fact, the angle $\phi$ calculated from equation (2), with the INDO parameters given in Table 2, is close ($\phi$ 10.6 ± 0.9°) to that obtained from equation (1) with its appropriate INDO parameters ($\phi$ 10.3 ± 0.7°), as well as to that estimated with the empirical parameters given earlier ($\phi$ 11.4°). The same is true for radical (I) whose $\phi$ values, calculated in the same way, are 4.6 ± 1.3, 4.7 ± 2.0, and 4.3°, respectively. Because of its complexity equation (2) is not of practical use, since one should always know the dependence of $a_{H\beta}$ upon $\phi$. However equation (2) can be rearranged into equation (3) that has only one empirical parameter and gives the conformation as a function of the difference ($\Delta a$) between the two experimental $a_{H\beta}$ splittings.

$$\phi = 1/2 \arcsin 2\Delta a/B'\sqrt{3} \qquad (3)$$

In the present case it yields $\phi$ 4.5 for (I) and 10.8° for (II) using the $B'$ values of Table 2; changes of $B'$ by as much as ±20% only affect the angle $\phi$ by ±2°. This means that even a very approximate knowledge of $B'$ allows a reliable conformational determination, whenever two different $a_{H\beta}$ values can be experimentally measured.

*Conclusions.*—We have found that radical (I) is in a symmetric (point group $C_2$) conformation whereas the analogous radical (II) is in a less symmetric (point group $C_s$) conformation. The two radicals, most likely, adopt an *anti*-conformation, with the C–X bond (X = $Me_3Si$ or MeS) rotated, with respect to the $2p_z$ orbital of $\dot{C}H$ (eclipsed position), by 4 ± 1 for (I) and 11 ± 1° for (II), respectively. Arguments were also presented to support the hypothesis that the $\dot{C}H$–$CH_2$ rotation is conrotatory in (I) but disrotatory in (II), although in principle another model could also account for the different e.s.r. features of these two radicals. Theoretical evidences also suggest that the lowering of the β-H methylene splittings in sulphur-containing radicals might depend on the electronic properties of the sulphur atom rather than on the geometrical distortion proposed in the literature.[2] As a consequence the well known relationship (1) seems adequate to describe the conformation of sulphur-containing radicals, as well as that of other radicals, although a more complete equation should, in principle, be considered.

## EXPERIMENTAL

3-Trimethylsilyl- and 3-methylthio-propene were commercially available products. Radical (I) was obtained by photolysis of $Bu^tOOBu^t$ and $Me_3SiH$ in the presence of $Me_3SiCH_2CH=CH_2$ (ratio 1 : 3 : 3 v/v) and (II) by photolysis of MeSSMe in the presence of $MeSCH_2CH=CH_2$ (ratio 1 : 2 v/v) both in cyclopropane as solvent.

The samples were prepared using a vacuum line and sealed in Suprasil quartz tubes. A 500 W mercury lamp was employed to photolyse the samples within the e.s.r. cavity; a water filter was used to absorb some of the heat from the light source.

The temperature was monitored by means of an iron–constantan thermocouple inserted in a dummy tube after each spectral determination; the accuracy is estimated to be ±5 °C and this error affects the $\Delta G^{\ddagger}$ values by ±0.1 kcal $mol^{-1}$.

The values of $\Delta G^{\ddagger}$ were the average of the measurements in the temperature range −150 to −100 °C; no attempt was made to obtain an Arrhenius plot in that the determination of both temperatures and rate constants were not of sufficient accuracy.

The INDO calculations were carried out with the classical program of Pople and Beveridge modified to introduce the second row elements: the new parameters introduced are those proposed by Benson and Hudson.[20]

The *ab initio* calculations were performed by means of the program Gaussian 70 (level STO 4-31 G).[25]

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