Rotational Barriers in Thienyl Triethylsilyloxy Nitroxides

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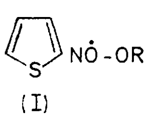
Triethylsilyloxy nitroxide radicals of thiophen and thienothiophens have been produced from the corresponding nitro-derivatives. Their e.s.r. spectra showed the presence of rotational isomers at low temperature for the thiophen radicals and even at room temperature for the thienothiophen analogues. In the former case the kinetics of the interconversion could be followed by examining variations in the line shape with temperature. The activation parameters have been determined and the rotational barrier is larger for the 2-thienyl than for the 3-thienyl silyloxy nitroxide. For the purpose of comparison the parameters related to the internal rotation of phenyl triethylsilyloxy nitroxide have been obtained.

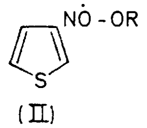
A VARIETY of 2-substituted thiophen derivatives has been investigated during the last few years to collect evidence on the existence of restricted rotation. The results have not been completely successful for a number of diamagnetic molecules, as in no case could the interconversion rate between two conformers be slowed enough to detect, even at low temperature, the individual species.[1-5]

The situation is somehow different for paramagnetic thiophen derivatives, since in this case species interconverting with rate constants as high as 10^5 s^{-1} can still give rise to individual e.s.r. signals. In many cases conformational isomers have been observed in anion [6] and cation [7] radicals of 2-substituted thiophens and one example of restricted rotation is known in the neutral 2-thenyl and 3-thenyl radicals.[8] In the ketyl radicals of thiophen and thienothiophens the rotational barriers have also been determined by a line shape study at different temperatures.[9] We report here the results of an e.s.r. investigation of 2- (I) and 3-thienyl (II), 2-thieno[3,2-*b*]thienyl (III), 2-thieno[2,3-*b*]thienyl (IV), and phenyl (V) triethylsilyloxy nitroxides.

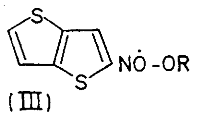
Even though nitroxide radicals have been under investigation for a long time, only recently was a nitroxide containing the thiophen ring obtained during the photolysis of 2-nitrothiophen in hydrogen donor solvents.[10] The room temperature e.s.r. spectrum is attributable to a single species ($2\text{-}C_4H_3S\text{-}N\dot{O}\text{-}OR$), no evidence of rotational isomers being reported. However some cases are known of nitroxides exhibiting restricted rotation; in particular in phenyl nitroxide [11] the *ortho*-protons become non-equivalent at −20° and some aliphatic nitroxides show linewidth alternation due to interconversion of the splitting of α-methylene protons.[12] In principle, therefore, we should expect that rotational isomers could be detected in thiophen nitroxides. We thus performed the experiments of ref. 10 in a different solvent at low temperature and observed different signals attributable to conformers having the nitroxide oxygen *cis* or *trans* to the heterocyclic sulphur atom.



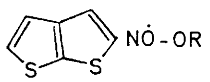
(I)



(II)

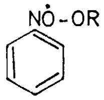


(III)



(IV)

R = SiEt$_3$



(V)

We have carried out a kinetic investigation of the isomer interconversion in the two thiophen nitroxides (I) and (II) and also of the internal rotation of the phenyl nitroxide (V) with the aim of gaining new information on the properties of these radicals.

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[7] C. M. Camaggi, L. Lunazzi, and G. Placucci, *J.C.S. Perkin II*, 1973, 1491.

[8] A. Hudson, H. A. Hussain, and J. W. E. Lewis, *Mol. Phys.*, 1968, **16**, 519.

[9] G. F. Pedulli, M. Tiecco, A. Alberti, and G. Martelli, *J.C.S. Perkin II*, 1973, 1816; M. Guerra, G. F. Pedulli, M. Tiecco, and G. Martelli, *ibid.*, 1974, 562.

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[11] Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Letters*, 1967, 1841.

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TABLE 1

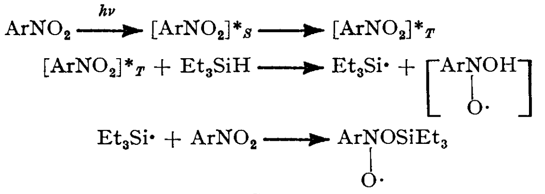
Hyperfine splitting constants (G) of the radicals (I)—(VI), and differences (ΔB_0/G) between the resonant fields of the spectral centres of the more stable and the less stable rotamer for radicals (I)—(IV)

Radical		a_N	$a_{2\text{-H}}$	$a_{3\text{-H}}$	$a_{4\text{-H}}$	$a_{5\text{-H}}$	$a_{6\text{-H}}$	ΔB_0
(Ia)	(55%)	13·32		5·58	1·15	4·73		0·025
(Ib)	(45%)	13·49		5·65	1·06	4·58		
(IIa)	(35%)	15·25	5·00		1·20	0·65		−0·25
(IIb)	(65%)	15·00	4·96		1·25	0·50		
(IIIa)	(60%)	12·65		6·17		2·86	0·78	0·035
(IIIb)	(40%)	12·85		6·07		2·78	0·77	
(IVa)	(65%)	13·50		6·40		0·55		0·05
(IVb)	(35%)	13·60		6·30		0·65		
(V)		14·76	3·20	1·04	3·10	1·04	3·10	
(VI) *		8·90	2·89	$1{\cdot}02_4$	3·24	$1{\cdot}02_4$	3·14	

* The a_H splitting of the hydrogen in the NHO group was 12·05 G.

RESULTS AND DISCUSSION

Rotational Isomerism.—The radicals from 2- and 3-nitrothiophen were generated by photolysis in triethylsilane. By assuming that triethylsilane behaves as the solvents used in ref. 10, the reaction sequence and the structure of the radicals † should be as shown in the Scheme.



$$ArNO_2 \xrightarrow{h\nu} [ArNO_2]^*_S \longrightarrow [ArNO_2]^*_T$$

$$[ArNO_2]^*_T + Et_3SiH \longrightarrow Et_3Si\cdot + \left[\begin{matrix}ArNOH\\ |\\ O\cdot\end{matrix}\right]$$

$$Et_3Si\cdot + ArNO_2 \longrightarrow \begin{matrix}ArNOSiEt_3\\ |\\ O\cdot\end{matrix}$$

SCHEME

Triethylsilane was preferred to other substrates since it gives spectra with a better signal to noise ratio because of its greater hydrogen donor ability; furthermore the spectra also have a reduced number of lines because of the lack of hydrogen atoms directly bonded to silicon.[10]

However, when an aromatic group containing two condensed rings, *e.g.* thieno[2,3-*b*]thienyl and thieno[3,2-*b*]thienyl, is examined, reaction under these conditions fails to give the corresponding nitroxides (III) and (IV). These radicals could nevertheless be obtained by addition of t-butyl peroxyoxalate to the solution.[13]

At room temperature the e.s.r. spectra of (I) and (II) show coupling of the unpaired electron with the nitrogen atom and three non-equivalent protons, indicative of the averaged spectrum. The assignment of the proton splittings was made by analogy with the similar trithienylmethyl and dithienylketyl radicals.[9,14,15]

On lowering the temperature some peaks begin to broaden, then split into new lines. These sharpen again until finally (at *ca.* −40°) the spectra of the *cis*- (a) and *trans*- (b) isomers, which have similar couplings (Table 1) and slightly different *g* values, are distinguishable (Figure 1).

Unfortunately it was not possible to find any experimental method for deciding which spectrum corresponds to the *cis*- and which to the *trans*-isomer. Some indication however can be obtained by following the suggestion of Hudson and Lewis for assigning the

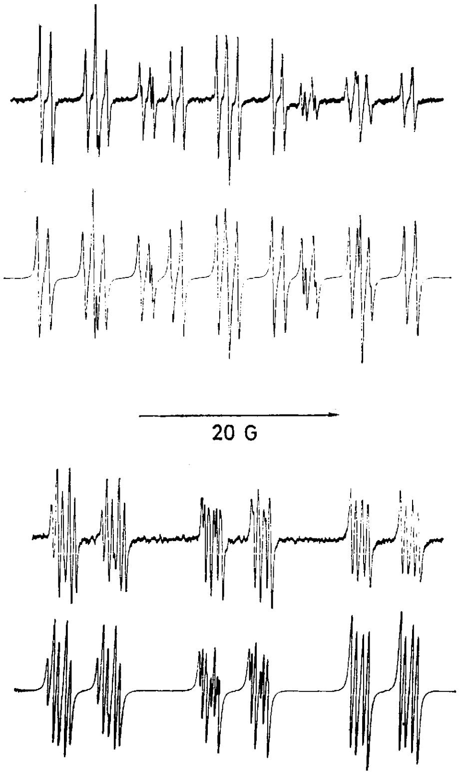
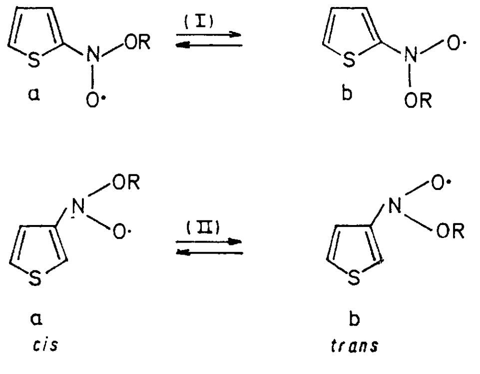


FIGURE 1 Experimental and computer simulated spectra of (I) (above) and (II) (below) at *ca.* −45° in the absence of exchange broadening



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† Attempts to detect satellite peaks of ^{29}Si failed owing to an inadequate signal to noise ratio.

[13] C. M. Camaggi, R. Leardini, and G. Placucci, *J.C.S. Perkin II*, 1974, 1195.

[14] A. Mangini, G. F. Pedulli, and M. Tiecco, *Tetrahedron Letters*, 1968, 4941; *J. Heterocyclic Chem.*, 1969, **6**, 721.

[15] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.

isomers of ketyl radicals and which has been experimentally verified in some cases.[6,15] They suggested that the larger spin densities are to be expected on the atom *trans* to the carbonyl oxygen. As the carbon in ketyls is isoelectronic with nitrogen in nitroxides we may assume that the same rule can be applied also in this case. Therefore in radical (I) the more stable isomer, having the larger value for $a_{3\text{-H}}$, should correspond to the *cis*-structure (Ia) and for the same reason the *trans*-isomer (IIb) should be the more stable conformer in radical (II).

Analogous behaviour with regard to rotational isomerism is expected for the thienothienyl nitroxides (III) and (IV) which, even at room temperature, show both isomers (Figure 2). Attempts to determine the coalescence point failed as the radicals quickly decay on raising the temperature.

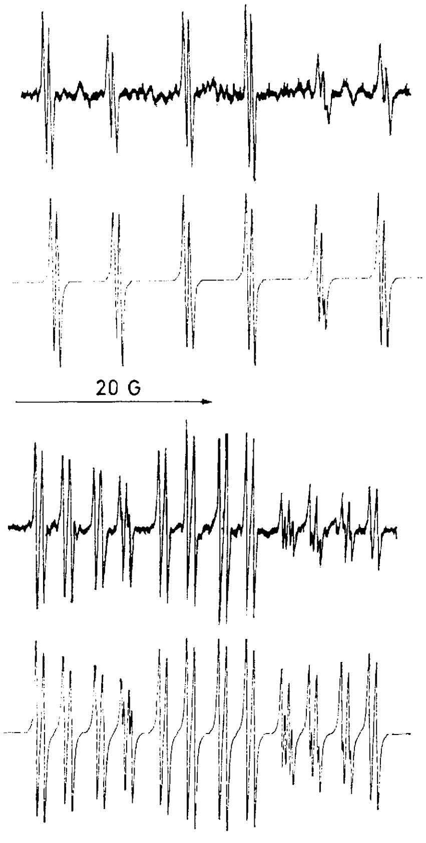

FIGURE 2 Experimental and computer simulated spectra of (III) (below) and (IV) (above) at room temperature

In this case also the *cis*-form is the preferred isomer. It should be pointed out that in carbonyl derivatives of thiophen this conformation is the more stable.[6,15,16]

The nitrogen splitting constants may yield useful information on the electron-withdrawing properties of the aromatic groups investigated; the larger the delocalizing power of the ring, the smaller the expected spin density at the nitrogen atom.

If one accepts the hypothesis that the contribution of the spin density of oxygen to the nitrogen splitting is similar in all the derivatives examined, we should observe smaller a_N values for the groups with the larger electron-attracting power. Since the trend of these splittings is 12·75, 13·40, 13·55, 14·74, and 15·95 G for (III), (I), (IV), (V), and (II) respectively we can establish the following sequence for the conjugative properties of the rings involved: 2-thieno[3,2-*b*]thienyl > 2-thieno-[2,3-*b*]thienyl ~ 2-thienyl > phenyl > 3-thienyl. An analogous pattern has been also found for many other radicals containing the same aromatic nuclei.[6,9,15]

Rotational Barriers.—Only in the case of radicals (I) and (II) could line shape analysis at various temperature be performed, while in the phenyl derivative (V) the non-equivalence of the *ortho*-protons is too small to be detected and both (III) and (IV) decay before any line width broadening is observed.

The line shape variations in (I) and (II) have been analysed using the density matrix theory, as previously reported.[9,17] *cis–trans*-Isomerisation was described by a two non-equivalent sites model with exchange rates k_1 and k_{-1}, where k_1 is the rate constant for the conversion of the more stable into the less stable species.

Owing to the asymmetric line width broadening which depends on the nuclear quantum number of nitrogen, we performed the line shape study only in the low field group of lines corresponding to the nitrogen quantum number m_I +1. Furthermore the spacing between lines corresponding to the two isomers is larger in this group, thus enhancing the accuracy of the determination. The ratio of the two isomers in (I) and (II) was measured from the relative height of the peaks as a function of temperature below —40° since in this region the rotation rate is too low to contribute to the line width. In the case of (I) no appreciable variation of the conformer ratio was observed while the relative amount of the *cis*-conformer of (II) was found to increase at low temperature. By measuring the equilibrium constants for the forward *trans* $\rightleftarrows$ *cis* isomerisation the thermodynamic quantities ΔH_0 and ΔS_0 were determined as 0·8 kcal mol^{-1} and 2·2 cal mol^{-1} K^{-1} respectively. The ratio of the conformers in the range of temperatures where exchange occurs was obtained by extrapolation using these values. The determination of the rate constants for the rotational process was made by comparing simulated and experimental spectra. Figure 3 shows the temperature dependence of the low field part of the experimental spectra of (II) together with the corresponding simulation. Figure 4 reports the Arrhenius diagram for the kinetic process involving (I) and (II) while Table 2 collects the activation parameters and the thermodynamic constants for the activated complex obtained from the Eyring equation assuming a transmission coefficient of unity. These quantities and the related standard errors have been calculated from the rate constants by the conventional least-square procedure.

The activation energy in the 2-thienyl derivative (I) (11·8 kcal mol^{-1}) is larger than in the corresponding

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[16] L. Lunazzi and C. A. Veracini, *J.C.S. Perkin II*, 1973, 1739.

[17] M. Guerra, G. E. Pedulli, and M. Tiecco, *J.C.S. Perkin II*, 1973, 903.

3-substituted derivative (II) (9·7 kcal mol^{-1}). This is in agreement with the greater conjugative properties of the 2- than the 3-thienyl group, which implies a larger double bond character between the nitroxide function and the aromatic ring. This behaviour confirms what is predicted on the basis of the relative values of the nitrogen splittings. Also the behaviour of the nitroxides (III) and (IV), where the rotation of the thienothiophen rings is so slow that no line broadening could be detected even at room temperature, can be now explained. In fact, from the proportionality between the energy barrier and the electron-withdrawing power of the ring, we would predict, for these two radicals, barriers to rotation relatively larger than in the corresponding thienyl derivatives and thus much smaller rate constants, as observed in the analogous ketyl radicals.[9]

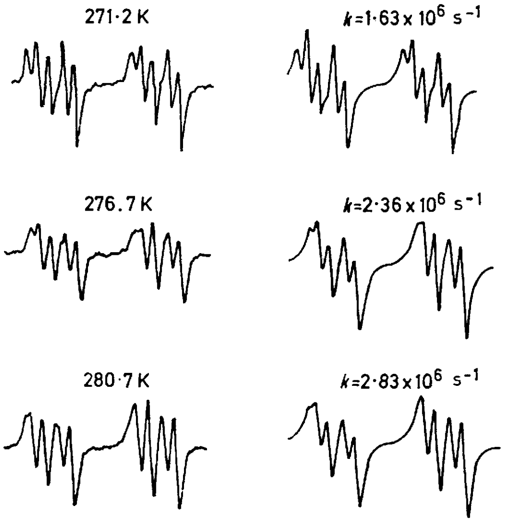

FIGURE 3 Experimental (left) and computer simulated (right) portion (low field region; $m_I = +1$) of the spectrum of (II) at three sample temperatures in the exchange broadening region

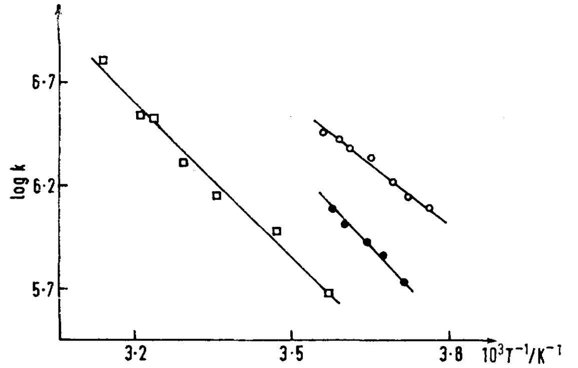

FIGURE 4 Arrhenius plot of radicals (I) (●), (II) (○), and (VI) (□). For (I) and (II) the log k values refer to the conversion from the more stable into the less stable isomer

TABLE 2

Activation parameters obtained for the conversion from the more stable into the less stable isomer in the radicals (I), (II), and (VI)

Radical	E_a/ kcal mol^{-1}	log A	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal mol^{-1} K^{-1}
(I)	11·78 ± 0·16	15·30 ± 0·13	11·23 ± 0·16	9·61 ± 0·58
(II)	9·74 ± 0·45	14·06 ± 0·36	9·16 ± 0·45	3·86 ± 1·65
(VI)	11·68 ± 0·51	14·77 ± 0·37	11·14 ± 0·52	7·22 ± 1·72

On the other hand the activation entropies in both radicals deviate from the zero value one would expect for a simple first-order rotational process.[18] In fact the two values are 9·5 ± 1·5 and 3·8 ± 2 cal mol^{-1} K^{-1} for (I) and (II) respectively, and although not exceedingly large, nevertheless deserve comment.

Positive $\Delta S^\ddagger$ values reflect a larger motional freedom in the transition with respect to the initial state.[18] A possible explanation may be the presence of the bulky aliphatic chain which in the ground state, because of larger steric hindrance, would experience greater restrictions to rotation around the nitrogen–oxygen bond than in the transition state, where the nitroxide function becomes orthogonal to the aromatic ring. If this is the case a negligibly small activation entropy should be expected for the internal rotation of nitroxides without aliphatic chains.

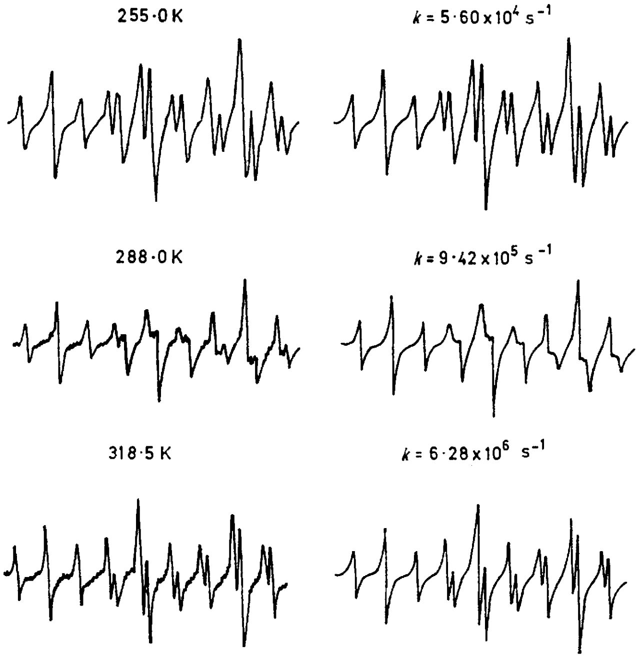

FIGURE 5 Experimental (left) and computer simulated (right) partial spectrum of (VI) (low field region) at three sample temperatures in the exchange broadening region

A well known radical which meets this requirement is phenyl nitroxide (VI); we have thus examined this radical which is generated by reaction of nitrosobenzene and phenylhydroxylamine.[11] Phenyl nitroxide has been reported [11] as having, at low temperature, two different a_H values for the two *ortho*-hydrogens (one of them, however, being equal to that of *para*-hydrogen). Careful simulation of the spectral shape shows that in (VI) all three splittings from the *ortho*- and *para*-hydrogens are different at low temperature (see Table 1). The 3·14 G splitting could be unambiguously assigned to the *para*-position by examination of the lines that did not exhibit broadening effects (Figure 5).

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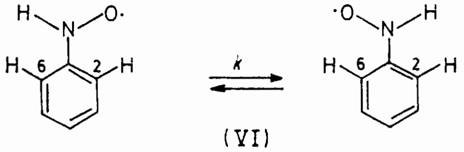
[18] B. G. Gowenlock, *Quart. Rev.*, 1960, **14**, 132.

The kinetic study on this radical must be performed in ethyl alcohol since the reactants are sparingly soluble in Et_3SiH; nevertheless the change of solvent should not greatly affect the intramolecular rotation. The rate constants were determined at various temperatures by following the modification of the spectral shape (Figure 5) due to the interconversion of the *ortho*-splittings. The result of these measurements yielded an activation energy of 11·7 kcal mol^{-1} and an entropy change of 7·2 cal mol^{-1} K^{-1} (Table 2); the latter value is different from zero, as in thienyl radicals (I) and (II), thus suggesting that the $OSiEt_2$ group is not, in the main, responsible for the deviation of the activation entropy from the ' normal ' value.



(VI)

A new hypothesis is therefore required and we tentatively suggest that the positive $\Delta S^‡$ values depends on the presence of the nitroxide group and is connected with the possibility of pyramidal inversion at the nitrogen in the transition state. Though aliphatic nitroxides are known from *X*-ray investigations to be pyramidal,[19] aromatic nitroxides are more likely to be planar because of conjugation.[20,21] The rotational process of (I), (II), and (VI) thus implies the passage from an initial planar state to a transition state where the aromatic ring is twisted by *ca.* 90° out of its original plane. In this transition state conjugation between the ring and the nitroxide group is prevented as in the aliphatic derivatives, and therefore the nitroxide group loses its planarity. Accordingly pyramidal inversion at the nitrogen, with a gain in the degree of freedom, is possible if the barrier to inversion is much smaller than the barrier to rotation.

Partial support for this hypothesis is given by INDO calculations performed on the simplest nitroxide ($H_2NO\cdot$) by minimizing the total energy with respect to all the geometrical parameters. The energy barrier to inversion calculated as the difference between the more stable pyramidal conformation and the planar transition state was calculated to be only 2·1 kcal mol^{-1}.

EXPERIMENTAL

The nitroxides were prepared as described in the literature.[22]

E.s.r. spectra were recorded on both Varian 4502 and JEOL JES-ME-IX instruments equipped with standard variable temperature devices. The temperature was measured before and after each scan by means of a chrome–alumel thermocouple placed in the Dewar insert just above the sensitive part of the cavity. The quartz tubes containing the samples were degassed. Particular care was taken in measuring the spectral line width in the absence of exchange broadening.

Photolyses were carried out with a Xenon 1000 W lamp without any particular focusing apparatus.

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[20] E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177; T. S. Lin, *J. Chem. Phys.*, 1972, **57**, 2260.

[21] A. W. Hanson, *Acta Cryst.*, 1953, **6**, 32.

[22] F. Challenger and R. Emmott, *J. Inst. Petroleum*, 1948, **34**, 922; B. Ostman, *Acta Chem. Scand.*, 1968, **22**, 1687.