

## An Investigation into the Effects of Chirality upon Electron Spin Resonance Spectra

By **Bruce C. Gilbert** \* and **Michael Trenwith**, Department of Chemistry, University of York, Heslington, York YO1 5DD

E.s.r. spectra are described for a series of nitroxides  $RCH_2N(Bu^t)O\cdot$  in which the group R comprises a carbon atom with three different substituents. As a result of this asymmetry the methylene hydrogen atoms are normally rendered magnetically non-equivalent and a quartet results: the recognition of this is clearly of diagnostic value. Further, deductions about molecular conformation can be made from the  $\beta$ -H splittings in each such chiral radical, and both solvent and temperature effects can to a certain extent be rationalised.

In a recent e.s.r. study of the utility of the nitromethane *aci*-anion as a spin-trapping agent for organic radicals in aqueous solution,<sup>1</sup> attention was drawn to the spectra of nitro-anion-radicals of the general type  $XYZCCH_2NO_2^-$ , obtained by scavenging a variety of carbon radicals which have three different substituents. In particular, for each of these anion-radicals two separate  $\beta$  (methylene) hydrogen splittings were resolved; this phenomenon, it was proposed, results from the presence in these species of an adjacent chiral centre, rather than from restriction of rotation.

We now report the e.s.r. spectra of a related series of radicals  $[XYZCCH_2N(Bu^t)O\cdot]$ , the preparation of which has been facilitated by the use of the spin-trap *N*-methylene-*t*-butylamine *N*-oxide,  $CH_2=N(Bu^t)O$ .<sup>2</sup> We have thus been able to extend the range of radicals in which a methylene group is flanked by a radical centre and an asymmetric carbon atom, and in all cases the appropriate hydrogen atoms can be demonstrated to be magnetically non-equivalent. In contrast to the anion-radicals discussed above, which were prepared in an aqueous flow-system, the nitroxides have been generated by continuous photolysis of static solutions. The comparative stability of nitroxides together with the relative convenience which the latter technique affords has enabled a detailed study of chiral radicals to be undertaken for a variety of solvent systems and at different temperatures.

Non-equivalence of this type in e.s.r. spectra has been hitherto recognised in only a few instances (*e.g.* for some simple nitroxides<sup>3</sup> and nitronyl nitroxides<sup>4,5</sup> in addition to nitro-anion-radicals<sup>1</sup>); however, we believe both that the effects of chirality may well be more widespread than is generally appreciated (further examples will be discussed later) and that an awareness of them can be a valuable aid to radical recognition. Of course, examples of chiral effects of this type in n.m.r. spectroscopy are well documented.<sup>6</sup> However, n.m.r. studies as detailed as we have been able to carry out for radicals using e.s.r. spectroscopy appear to be uncommon. This is probably

<sup>1</sup> B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

<sup>2</sup> G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 401.

<sup>3</sup> E. Flesia, A. Croatto, P. Tordo, and J.-M. Surzur, *Tetrahedron Letters*, 1972, 535.

<sup>4</sup> R. W. Kreilick, J. Becher, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1969, **91**, 5121.

<sup>5</sup> R. J. Weinkam and E. C. Jorgensen, *J. Amer. Chem. Soc.*, 1971, **93**, 7028, 7033.

a consequence of inherent difficulties in the choice of suitable compounds with appreciable chemical shift differences between the relevant nuclei.

### EXPERIMENTAL

Spectra were recorded on a Varian E3 spectrometer equipped with 100 kHz modulation and an X-band klystron. A V-4540 variable temperature accessory was employed for work at other than ambient temperature, and the temperature of each sample was measured to within  $\pm 2^\circ$  with a thermocouple. Hyperfine splittings were measured to within  $\pm 0.006$  mT (unless otherwise stated) by comparison with the spectra from an aqueous solution of Fremy's salt [ $a(N) = 1.3091 \pm 0.0004$  mT<sup>7</sup>] and from a solution of *p*-benzosemiquinone in aqueous ethanol [ $a(H) = 0.2368 \pm 0.0001$  mT<sup>8</sup>].

*N*-Methylene-*t*-butylamine *N*-oxide was prepared as an ethereal solution from 2-methyl-2-nitrosopropane (obtained from *t*-butylhydroxylamine<sup>9</sup>) and diazomethane<sup>10</sup> using a modification of the method of Baldwin *et al.*,<sup>11</sup> whereby the nitroso-dimer was used without fusing. Starting materials were commercial samples which were used without further purification.

Suitably substituted radicals were generated by continuous photolysis of solutions containing hydrogen peroxide (100 volume), di-*t*-butyl peroxide (purified on a basic alumina column), benzophenone, or potassium persulphate, together with a suitable hydrogen donor, or (with the persulphate experiments) a carboxylic acid, using a 400 W Hanovia medium pressure mercury arc lamp. Each solution also contained the nitron spin-trap (produced by removal of ether), at concentrations between 0.02 and 0.1M, and was deoxygenated with a nitrogen purge prior to irradiation. When photolysis was discontinued, the nitroxide radicals were observed to decay fairly quickly ( $\tau_{\frac{1}{2}}$  ca. 2 min). Spectra sometimes contained signals from secondary radicals the nature of which was not always established.

### RESULTS

(a) *Assignments of Spectra*.—We have chosen substrates for reaction which should preferentially yield radicals in which the tervalent carbon atom is substituted with three

<sup>6</sup> M. L. Martin and G. J. Martin, *Bull. Soc. chim. France*, 1966, 2117; M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 14.

<sup>7</sup> R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

<sup>8</sup> M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 1350.

<sup>9</sup> W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 6522.

<sup>10</sup> Th. J. de Boer and H. J. Backer, *Rec. Trav. chim.*, 1954, **73**, 229.

<sup>11</sup> J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc. (C)*, 1969, 1073.

different groups. In Table 1 are the hyperfine splittings for a variety of nitroxides formed by trapping with the nitron at room temperature; spectra were obtained from hydrogen donors (*e.g.* alcohols and ethers) with  $\cdot\text{OH}$ ,  $\cdot\text{O}^t\text{Bu}$ , and triplet benzophenone, and also, in some cases, from  $\text{SO}_4^{\cdot-}$ . Details have been included for two separate solvent systems for most radicals in order to illustrate the nature of the solvent effects observed (see later).

ation of the non-equivalence, nor can we observe it [for radicals (1)—(3) and (5); (4) does show the effect] under their conditions (1M-alcohol in benzene). Although this may be partly because of the appearance of signals from  $\text{Bu}^t_2\text{NO}\cdot$  in this solvent system we also believe it to be a real effect. On increasing the alcohol concentration for benzene solutions or when aqueous hydrogen peroxide is used, the non-equivalence becomes quite unambiguous and better

TABLE 1  
Hyperfine splittings (mT) for nitroxide radicals (1)—(13) of the type  $\text{XYZCCH}_2\text{N}(\text{Bu}^t)\text{O}\cdot$

Substrate	Method of generation <sup>a</sup>	Radical	X	Y	Z	$a(\text{N})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$	$\Sigma a(\beta\text{-H})$	$\Delta a(\beta\text{-H})$
Ethanol	$\text{H}_2\text{O}_2$	(1)	H	Me	OH	1.641	0.913, 1.328	0.051	2.241	0.415
	$\text{Ph}_2\text{C}=\text{O}$					1.603	0.975, 1.195	0.051	2.170	0.220
Propanol	$\text{H}_2\text{O}_2$	(2)	H	Et	OH	1.639	0.875, 1.356	0.049	2.231	0.481
	$\text{Ph}_2\text{C}=\text{O}$					1.616	0.947, 1.250	0.049	2.197	0.303
Butanol	$\text{H}_2\text{O}_2$	(3)	H	Pr	OH	1.669	0.825, 1.430	0.044	2.255	0.605
	$\text{Ph}_2\text{C}=\text{O}$					1.604	0.934, 1.265	0.054	2.199	0.331
Isobutanol	$\text{H}_2\text{O}_2$	(4)	H	Pr <sup>i</sup>	OH	1.697	0.752, 1.526	0.062	2.278	0.774
	$\text{Ph}_2\text{C}=\text{O}$					1.621	0.904, 1.306	0.039	2.210	0.402
Benzyl alcohol	$\text{Ph}_2\text{C}=\text{O}$	(5)	H	Ph	OH	1.610	0.989, 1.205	0.048	2.194	0.216
Ethylene glycol	$\text{H}_2\text{O}_2$	(6)	H	$\text{CH}_2\text{OH}$	OH	1.638	0.813, 1.425	0.063	2.238	0.612
	$\text{Ph}_2\text{C}=\text{O}$					1.619	0.859, 1.345	0.040	2.204	0.486
Butane-2,3-diol	$\text{H}_2\text{O}_2$	(7)	Me	$\text{CHMeOH}$	OH	1.644	2.256 <sup>b</sup>		2.256	<i>b</i>
	$(\text{Bu}^t\text{O})_2$ <sup>c</sup>					1.569	2.194 <sup>b</sup>		2.194	<i>b</i>
Diethyl ether	$\text{Ph}_2\text{C}=\text{O}$	(8)	H	Me	OEt	1.510	0.698, 1.235		1.933	0.537
	$\text{H}_2\text{O}_2$	(9)	H	$\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$		1.644	0.788, 1.433	0.050	2.221	0.645
1,4-Dioxan	$\text{Ph}_2\text{C}=\text{O}$					1.538	0.736, 1.191	0.054	1.927	0.455
	$\text{H}_2\text{O}_2$	(10)	H	$\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$		1.637	0.768, 1.339		2.107	0.571
Tetrahydrofuran	$\text{Ph}_2\text{C}=\text{O}$					1.520	0.709, 1.153		1.862	0.444
	$\text{H}_2\text{O}_2$					1.531	0.669, 1.313	0.050	1.982	0.644
Ethyl acetate	$\text{SO}_4^{\cdot-}$ <sup>d</sup>	(11)	H	Me	OAc	1.644	0.681, 1.444	0.069	2.125	0.763
Chloroacetic acid	$\text{SO}_4^{\cdot-}$ <sup>d</sup>	(12)	H	Cl	$\text{CO}_2^-$	1.644	0.681, 1.444	0.069	2.125	0.763
2-Chloropropionic acid	$\text{SO}_4^{\cdot-}$ <sup>d</sup>	(13)	H	Cl	Me	1.619	0.681, 1.380	0.050	2.061	0.699

<sup>a</sup> Unless stated otherwise, methods as follows: photolysis of substrate–100 volume  $\text{H}_2\text{O}_2$  1 : 2 (v/v); photolysis of solutions of benzophenone (0.01M) in substrates. <sup>b</sup> Inner lines too broad for exact measurement. <sup>c</sup> Photolysis of diol–di-*t*-butyl peroxide 1 : 2 (v/v). <sup>d</sup> Photolysis of aqueous solutions containing 2M-potassium persulphate and 5M-acid.

Under the conditions reported in Table 1, each radical exhibits two non-equivalent  $\beta$ -hydrogen splittings and the inside lines of the 1 : 1 : 1 : 1 pattern from these hydrogens are broader than the outside lines. This we believe to be typical for radicals with three different groups on the  $\gamma$ -carbon atom. For example, ethanol, propanol, butanol, isobutanol, and benzyl alcohol react with the priming radicals to give, in the presence of the trap, spectra assigned to the spin-adducts (1)—(5), respectively; the activating influence of the hydroxy-group towards hydrogen atom abstraction from the adjacent carbon is again confirmed.<sup>12</sup> The spectrum from radical (5) is shown in Figure 1. Ethylene glycol gives spectra ascribable to (6), as judged by the pattern from the  $\beta$ -hydrogen interaction. This suggests that the first formed radical ( $\cdot\text{CHOHCH}_2\text{OH}$ ) is rapidly scavenged before dehydration<sup>13</sup> (to  $\cdot\text{CH}_2\text{CHO}$ ); we could also detect (6) during the photolysis of hydrogen peroxide in the presence of allyl alcohol and 2-methyl-2-nitrosopropane. By analogy, the spectrum from butane-2,3-diol is assigned structure (7); in this and some other cases, pronounced broadening of the central lines precludes exact analysis and only the sum of the  $\beta$ -H splittings is then given. Janzen and Lopp have described<sup>14</sup> the spectra of some nitroxides  $\text{R}^1\text{R}^2\text{C}(\text{OH})\text{CH}_2\text{N}(\text{Bu}^t)\text{O}\cdot$ , including (1), (4), and (5), generated in similar fashion but under different solvent conditions. However, these authors do not report observ-

signals are observed. Further investigations are described in the next sections.

Diethyl ether and 1,4-dioxan, with all three hydrogen-abstracting systems, give the spectra of radicals (8) and (9),

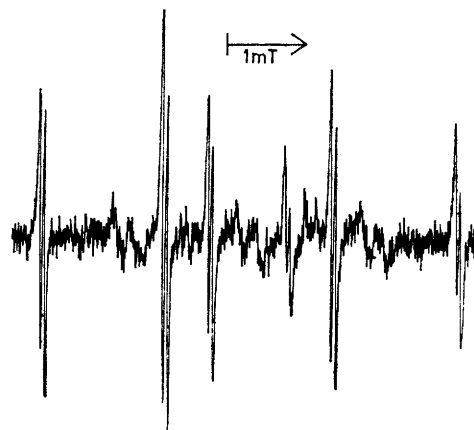


FIGURE 1 E.s.r. spectrum of the radical  $\text{PhCH}(\text{OH})\text{CH}_2\text{N}(\text{Bu}^t)\text{O}\cdot$

respectively. The spectrum from (9) is shown in Figure 2. The adduct from tetrahydrofuran is tentatively assigned structure (10) on the basis both of the methylene proton pattern [*cf.* (8) and (9)] and of the expected faster formation

<sup>14</sup> E. G. Janzen and I. G. Lopp, *J. Magnetic Resonance*, 1972, 7, 107.

<sup>12</sup> W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

<sup>13</sup> B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

of the  $\alpha$ - than the  $\beta$ -radical. For the ether-derived radicals, the nitrogen splittings are considerably greater for the aqueous rather than the ethereal environment, evidently by virtue of the stabilisation of the polar structure  $R_2\dot{N}^+-O^-$  in the latter case. In contrast, the alcohol-derived radicals show little decrease on going from an aqueous to an alcoholic

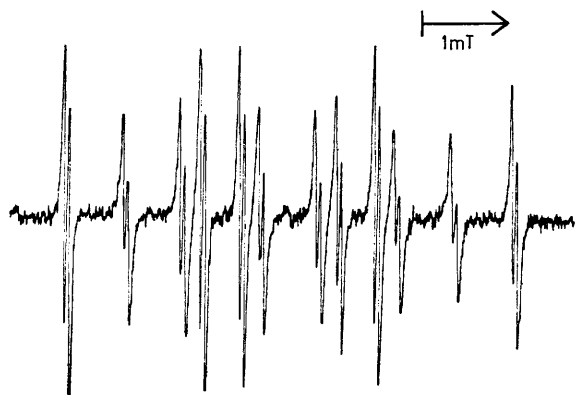


FIGURE 2 E.s.r. spectrum of the radical  
 $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCHCH}_2\text{N}(\text{Bu})\text{O}^\cdot$

solution. We regard this as evidence for either intra- or inter-molecular hydrogen bonding of the nitroxide oxygen atom in alcoholic solvents as well as in water. Studies over a range of solvent concentration (see later) provide corroborative evidence for the suggestion<sup>14</sup> that, at least for low alcohol concentrations in non-polar solvents (1M in benzene), the effects are intramolecular.

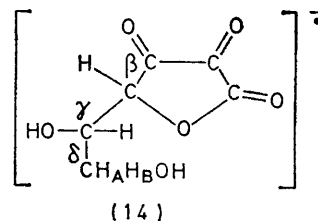
The recognition of non-equivalent  $\beta$ -hydrogen splittings in the radical produced by hydrogen atom abstraction from ethyl acetate with hydroxyl radical leads to the assignment of structure (11). Reaction of 2-chloropropionic acid with  $\text{SO}_4^{\cdot-}$ , generated photochemically from potassium persulphate, leads to the radical  $\cdot\text{CHMeCl}$ , as judged by the splittings from the resulting nitroxide, assigned structure (12). Although reaction in this case appears to lead to oxidative decarboxylation,<sup>1</sup> with chloroacetic acid the radical  $\cdot\text{CHClCO}_2^-$  is evidently formed *via* hydrogen abstraction.

Radicals which are trapped but which do not lead to the formation of nitroxides with asymmetric  $\gamma$ -carbons (and which hence lead to spectra with equivalent  $\beta$ -splittings) include  $\cdot\text{CH}_2\text{OH}$ ,  $\cdot\text{CMe}_2\text{OH}$  (see also ref. 14),  $\cdot\text{Me}$  and  $\cdot\text{Ph}$ ,<sup>2,14</sup>  $\cdot\text{Bu}^t$ ,<sup>14</sup> benzoyloxy, and succinimidyl.<sup>2</sup> These adducts and the chiral species can be readily distinguished, suggesting an advantage of *N*-methylene-*t*-butylamine *N*-oxide, compared with other nitrones, as a trap.

Appreciation of the effects of a chiral carbon atom on e.s.r. spectra can be diagnostically useful in other systems. For example, we have attempted to prepare hitherto unknown three-membered cyclic nitroxides by the oxidation of ethyleneimine and propyleneimine using standard procedures for secondary amines.<sup>15</sup> The spectra we observe are characterised by  $g = 2.0056$  and the following splittings: from ethyleneimine,  $a(\text{N}) = 1.550$  and  $a(4\text{H}) = 1.091$  mT, and from propyleneimine,  $a(\text{N}) = 1.538$  and  $a(1\text{H each}) =$

0.271, 0.838, and 1.327 mT. We assign the structures of the radicals not to cyclic products but to ring-opened nitroxides (probably polymerised) of the type  $-\text{CH}_2\text{CH}_2-\text{N}(\text{O})-\text{CH}_2\text{CH}_2-$  and  $-\text{CHMeCH}_2-\text{N}(\text{O})-\text{CHMeCH}_2-$ , respectively, with the latter exhibiting characteristic non-equivalent  $\beta$ -proton splittings of 0.838 and 1.327 mT from the  $\text{CH}_A\text{H}_B$  group between the nitroxide function and the adjacent chiral centre (*cf.* results in Table 1). Asymmetry at the  $\gamma$ -carbon, rather than restricted rotation about the  $\text{C}_\alpha-\text{C}_\beta$  bond (*i.e.* conformational interconversion in the slow exchange region), is probably also responsible for the observation of magnetically non-equivalent  $\beta$ -hydrogen coupling in the radicals  $\cdot\text{CMe}(\text{CO}_2\text{Me})\text{CH}_2[\text{CMe}(\text{CO}_2\text{Me})\text{CH}_2]_n\text{OH}$ <sup>16</sup> and  $\cdot\text{CMe}(\text{CO}_2\text{R})\text{CH}_2[\text{CMe}(\text{CO}_2\text{R})\text{CH}_2]_n\text{CMe}_2\text{CN}$ ,<sup>17</sup> detected during polymerisation of alkyl methacrylates and generated using transition metal-peroxide and photoinitiation methods, respectively. Moreover, in the latter case, the characteristic 1:broad:broad:1 pattern from the  $\beta$ -hydrogens is observed<sup>17</sup> to sharpen (not coalesce) as the temperature is raised. This is as we have found for the nitroxides and it indicates that the high temperature limit is 1:1:1:1; *i.e.*, that intrinsic asymmetry, rather than restricted rotation, causes the observed non-equivalence.

Instances where methylene hydrogens further removed from the radical centre can be affected by the presence of chiral groups may well also exist; in addition to an example already pointed out<sup>18</sup> [ $\text{CH}_3\text{CH}_A\text{H}_B\text{CH}(\text{PO}_3^{2-})\text{NO}_2^-$ ], we also believe that this phenomenon accounts for non-equivalence observed<sup>19</sup> for the radical  $\cdot\text{CH}(\text{CO}_2^-)\text{C}(\text{OH})(\text{CO}_2^-)\text{CH}_A\text{H}_B\text{CO}_2^-$  and may be implicated for the radical (14) derived from ascorbic acid.<sup>20</sup>



(b) *Solvent and Temperature Effects.*—In order to obtain more information about the factors upon which the nature of the spectra depend, we have examined the effect of solvent and temperature changes on the sums and differences of the two  $\beta$ -hydrogen splittings for a variety of chiral nitroxides, including both ether- and alcohol-derived radicals.

Figure 3 shows the variation of  $a(\text{N})$  and  $\Sigma a(\beta\text{-H})$  with the solvent composition as the amount of alcohol (for ethanol and benzyl alcohol) or ether (for dioxan) in benzene is varied; triplet benzophenone was used for radical generation. Although changes in  $a(\text{N})$  are slight, the effect on  $\Sigma a(\beta\text{-H})$  for the two alcohol-derived radicals is much more pronounced than that for the ether-derived nitroxide. Since the latter cannot participate in hydrogen bonding, it may be inferred that for the former radicals the effect stems from conformational changes resulting from variations in solvent composition (*e.g.* increased inter-, rather than intramolecular, hydrogen bonding at higher alcohol concentrations). Such behaviour may also account for the striking result that although there is a marked non-equivalence between the  $\beta$ -hydrogen splittings for alcohol radicals in

<sup>15</sup> E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177.

<sup>16</sup> H. Fischer, *J. Polymer Sci. B*, 1964, **2**, 529.

<sup>17</sup> P. Smith and R. D. Stevens, *J. Phys. Chem.*, 1972, **76**, 3141.

<sup>18</sup> B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, *J.C.S. Perkin II*, 1972, 1508.

<sup>19</sup> H. Zeldes and R. Livingston, *J. Amer. Chem. Soc.*, 1971, **93**, 1082.

<sup>20</sup> G. P. Laroff, R. W. Fessenden, and R. H. Schuler, *J. Amer. Chem. Soc.*, 1972, **94**, 9062.

aqueous solutions or at high alcohol concentrations (Table 1), the  $\beta$ -hydrogens for the alcohol radicals appear to be equivalent at low alcohol concentrations. We have confirmed this for (1)—(3), and (5) for 1M solutions; for (4) there is still a slight non-equivalence at this concentration. In contrast, the radical (9) demonstrates non-equivalence of its  $\beta$ -H splittings at all solvent conditions explored (aqueous and benzene solutions). We have studied in

pattern are greater than those of the outside lines and they also increase with decreasing temperature. For example, for radical (1) the ratios of the outer to the inner peak

TABLE 2

Dependence of  $\beta$ -hydrogen splittings (mT) for radicals (1) and (5) on concentration of hydrogen donor in benzene solution <sup>a</sup>

Radical	Mole fraction of donor alcohol in benzene	$a(\beta\text{-H})^b$
(1)	0.15	1.194(2) <sup>c</sup>
	0.28	1.167(2)
	0.50	1.091
		1.172
	0.70	1.047
	0.86	1.159
(5)		1.006
		1.163
	0.04	1.135(2)
	0.10	1.131(2)
	0.36	1.006
	0.56	1.209
	0.990	
	1.186	
	0.971	
	1.195	

<sup>a</sup> Temp. ca. 25°. <sup>b</sup>  $\pm 0.01$  mT for radical (5), reflecting the broadening of the middle line(s). <sup>c</sup> Two equivalent protons.

TABLE 3

Hyperfine splittings (mT) <sup>a</sup> for radicals (1) and (9) as a function of temperature <sup>b</sup>

Radical	T/°C	$a(\text{N})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$	$\Sigma a(\beta\text{-H})^c$	$\Delta a(\beta\text{-H})^d$
(1)	16	1.598	0.939, 1.236	0.064	2.175	0.297
	12	1.599	0.934, 1.240	0.065	2.174	0.306
	8	1.606	0.929, 1.255	0.066	2.184	0.326
	3	1.605	0.918, 1.263	0.066	2.181	0.345
	-3	1.605	0.908, 1.273	0.066	2.181	0.365
	-9	1.607	0.889, 1.281	0.067	2.170	0.392
	-12	1.602	0.861, 1.288	0.069	2.141	0.427
	-20	1.607	0.840, 1.318	0.068	2.158	0.478
	-23	1.604	0.815, 1.328	<i>d</i>	2.143	0.513
	-31	1.604	0.811, 1.335	<i>d</i>	2.146	0.524
	(9)	24	1.569	0.707, 1.284	0.057	1.991
10		1.572	0.691, 1.304	0.058	1.995	0.613
7		1.571	0.678, 1.312	0.059	1.990	0.634
-1		1.572	0.670, 1.324	0.059	1.994	0.654
-6		1.574	0.663, 1.336	0.059	1.999	0.673
-9		1.574	0.655, 1.338	0.061	1.994	0.683
-14		1.574	0.637, 1.356	0.059	1.993	0.719

<sup>a</sup>  $\pm 0.002$  mT. <sup>b</sup> Generated by photolysis of hydrogen peroxide-hydrogen donor 1 : 4 (v/v). <sup>c</sup> See text. <sup>d</sup> Expected  $\gamma$ -splitting unresolved.

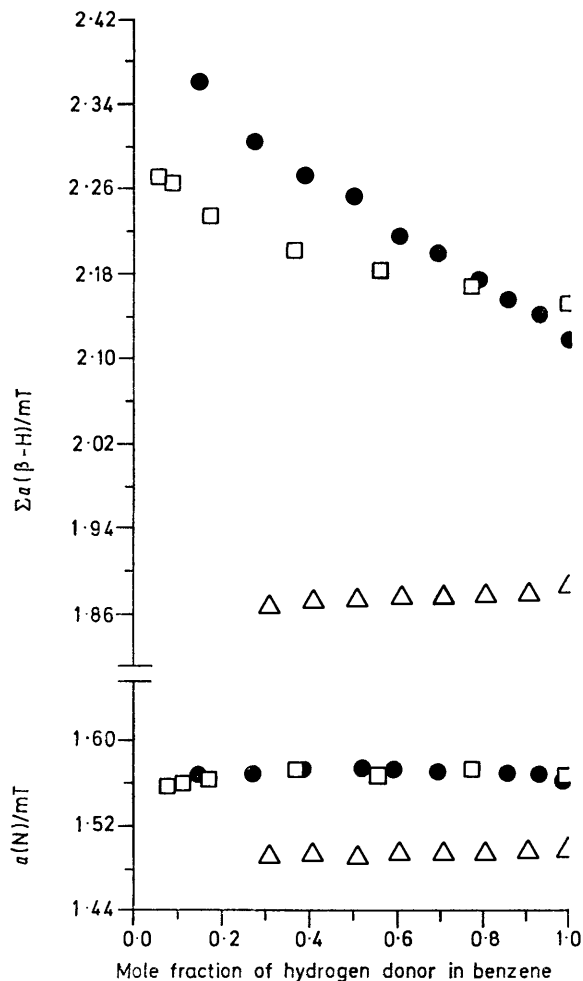


FIGURE 3 Variation of  $a(\text{N})$  and  $\Sigma a(\beta\text{-H})$  with concentration of hydrogen donor in benzene for radicals  $\text{XCH}_2\text{N}(\text{Bu}^t\text{O})\cdot$ :  $\bullet$ ,  $\text{X} = \text{CH}_3\text{CH}(\text{OH})$ ;  $\square$ ,  $\text{X} = \text{PhCH}(\text{OH})$ ; and  $\triangle$ ,  $\text{X} = \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}$

detail the behaviour of (1) and (5) for different concentrations of alcohol in benzene (with ca. 0.1M-benzophenone as radical initiator and nitron as the trap) and find that, in both cases, the non-equivalence of the  $\beta$ -splittings is induced by increasing the alcohol content (Table 2).

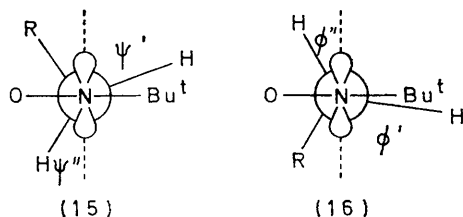
Table 3 contains the results at a series of temperatures for the spin-adducts of radicals derived from ethanol and 1,4-dioxan with the hydroxyl radical [with a ratio of substrate to hydrogen peroxide of 4 : 1 (v/v) in each case]. The sum of the  $\beta$ -splittings is seen to remain approximately constant through both series of measurements [as does  $a(\text{N})$ ]. The difference,  $\Delta a$ , increases quite markedly, however, with decreasing temperature. As explained above, the line-widths of the two inside lines of the methylene hyperfine

heights of the  $\Delta\tilde{M}_N = 0$  group of lines at 16 and  $-31^\circ$  are 1.70 and 2.86, respectively; for radical (9) the figures are 1.28 at 24 and 2.23 at  $-14^\circ$ . The width of the outer lines remains approximately constant (ca. 0.02 mT).

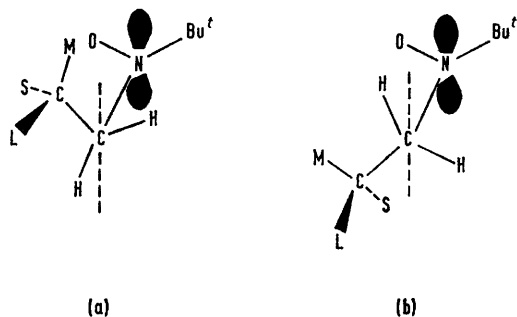
#### DISCUSSION

The origin of the characteristic four-line splitting pattern from the  $\beta$ -hydrogen atoms in radicals of the type  $\text{XYZCC}_2\text{N}(\text{Bu}^t\text{O})\cdot$  can perhaps best be understood with reference to a trapped adduct with three differently-sized groups, as in the following simplified picture. Consider first a possible minimum energy conformation for  $\text{RCH}_2\text{N}(\text{Bu}^t\text{O})\cdot$  with the two  $\beta$ -protons making dihedral angles  $\psi'$  and  $\psi''$  with the orbital of the unpaired electron

on nitrogen (and hence giving different splittings  $a_1$  and  $a_2$ ). This conformation is likely to be of the type (15) on the basis of results for achiral methylene nitroxides,<sup>15</sup> with the substituent avoiding the t-butyl group.



There is another similar conformation (16) with similar angles  $\phi'$  and  $\phi''$  (and splittings  $a_2'$  and  $a_1'$ ); however because R is chiral the spatial dispositions of the two hydrogens with respect to both the radical centre and the three groups on the  $\gamma$ -carbon are not the same in the two cases (Figure 4). This should mean that the splittings are not identical and also that the energies are not equal; either of these instances, or a combination of the two, leads to a 1:1:1:1 (*i.e.*, non-equivalent) pattern. We can illustrate the first of these possibilities by considering rapid interconversion of a 1:1:1:1 pattern into a quartet with different splittings (Figure 5). Fast interconversion still leads to a 1:1:1:1 pattern, as indicated by the averaged line-positions, because the two protons do not experience the same averaged environment or splitting (they are diastereotopic); for slower rates of interconversion all the lines should broaden, but since the broadening depends on the frequency difference between the lines being interconverted, the effect is greater for the inner pair. This is as observed, the broadening of the inner pair being greater at lower temperatures or when larger groups are substituted [*e.g.* (5) or (7)]. The second of the possibilities (non-equivalent  $\beta$ -hydrogens because of different



with methyl group equatorial is highly favoured, so that the resulting averaged spectrum resembles that expected for this conformer, with two different  $\beta$ -splittings.

We believe that for the chiral radicals considered here both effects play a part in creating the general phenomenon and also that spectra can be interpreted in terms both of the conformations preferred and of the relative weightings in different examples. Thus the sum of the hydrogen splittings at any moment will depend on  $\phi'$  and  $\phi''$  (or  $\psi'$  and  $\psi''$ ); this can be calculated from the  $B \cos^2 \theta$  relationship where  $\theta$  is the dihedral angle made between the  $C_\beta$ -H bond and the orbital of the unpaired electron (see, *e.g.* ref. 15). The magnitude of the sum should indicate, approximately, the angles in the (two)

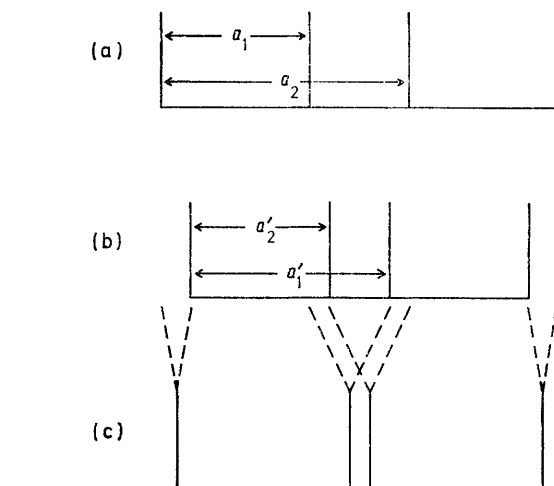


FIGURE 5 Expected methylene hyperfine splitting pattern from conformations (15) and (16), (a) and (b), respectively, with the averaged line positions (c)

preferred conformations. Now when the two more or less equivalent conformations have different energies, then the greater the weighting of one of these (*e.g.* as the temperature is lowered or when suitable steric effects are introduced) the more the spectrum should resemble the favoured conformer [*e.g.* Figure 5(a)]. This will be reflected in the difference between the  $\beta$ -splittings. Thus the spectra from chiral radicals contain potentially more information concerning conformational effects than does the single  $\beta$ -CH<sub>2</sub> splitting from an achiral radical, especially as line-broadening effects should be capable of yielding kinetic data. The remainder of the paper is devoted to our attempts to substantiate the simple theory and to derive conformational information.

The invariance of the sum of the  $\beta$ -splittings for the radicals (1) and (9) as the temperature is varied (Table 3) suggests that, for each radical, the favoured conformations represented have somewhat similar dihedral angles and hence similar sums for  $a(\beta\text{-H})$  and  $a(\beta\text{-H}')$ . Indeed, we can calculate which values of  $\theta'$  and  $\theta''$  give the required sum; this is achieved using the value<sup>22</sup> of 1.13 mT for the splitting from the freely rotating methyl

FIGURE 4 Two possible minimum energy conformations for a representative nitroxide  $\text{SMLCCH}_2\text{N}(\text{Bu}^t)\text{O}\cdot$  with three differently-sized substituents (small, medium, and large) on the  $\gamma$ -carbon atom

weightings of the two conformations considered) would also lead to the observed effect; a precedent here is given, for example, by the high temperature spectra observed for 4-methylpiperidyl nitroxide.<sup>21</sup> Although the two chair forms are rapidly interconverted, the one

<sup>21</sup> J. J. Windle, J. A. Kuhnle, and B. H. Beck, *J. Chem. Phys.*, 1969, **50**, 2630.

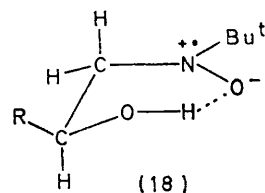
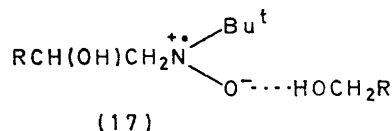
<sup>22</sup> M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 395.

group in  $\text{MeN}(\text{Bu}^t)\text{O}^\cdot$ , assuming a  $B\cos^2\theta$  relationship to hold in this and our examples. [Correction must be made to allow for the different values of  $a(\text{N})$ , and hence the spin density on nitrogen, in different solvents.] In this way we determine the average dihedral angle for the  $\text{CH}_3\text{CH}(\text{OH})$  group in (1) as  $40 \pm 5^\circ$ , with dihedral angles for the  $\beta$ -hydrogens as  $80 \pm 5$  and  $20 \pm 5^\circ$ ; since the large group will presumably avoid the *t*-butyl substituent, this suggests that (15) and (16), with approximately these angles, are the favoured conformations. It is also interesting to note that, for related radicals prepared under similar conditions, the values of  $\Sigma a(\beta\text{-H})$  are remarkably similar (*e.g.* for  $\text{RCH}_2\text{OH} + \cdot\text{OH}$  priming system,  $2.242 \pm 0.048$  mT); this suggests that for a variety of alcohol adducts the favoured conformations must exhibit a certain degree of similarity.

The increase in the difference between the  $\beta$ -splittings in either (1) or (9) as the temperature is lowered indicates that one of the non-equivalent conformations of favourable energy [*i.e.* (15) or (16)] is becoming increasingly populated at the expense of the other (though the constancy of the sum suggests similar angles in the two cases). It is also noteworthy that an increase in the size of the substituent on the  $\gamma$ -carbon atom similarly leads to an increase in  $\Delta a$ , presumably through increasingly disparate weighting of the two possible 'favoured' conformations [see, *e.g.*, values of  $\Delta a$  for (1)–(6); Table I]. Similar trends are apparent from substituent effects in the spectra<sup>1</sup> of analogous nitro-anion-radicals  $\text{XYZCCH}_2\text{NO}_2^{\cdot-}$ ; thus, the greatest differences  $\Delta a$  occur when one or more large groups is present.

The solvent effects for the alcohol-derived radicals are now understandable as follows. At high alcohol concentrations, open-chain radicals presumably dominate [*e.g.* (17)]; however, at low alcohol concentrations the proportion of cyclic species [*i.e.* (18) and the conformer obtained by ring-flipping] increases and eventually predominates. We can conclude, from Figure 3, that in the cyclic form the sum of the  $\beta$ -hydrogen splittings is greater than that for the open chain form; the spin density on nitrogen remains constant, as judged by the invariance of  $a(\text{N})$ . The dihedral angles which together would give  $\Sigma a(\beta\text{-H})$  as *ca.* 2.4 mT are  $75$  and  $15^\circ$ ; this is very close to that expected for the pseudo-axial and -equatorial protons in a six-membered ring such as (18), assuming that the nitroxide function is planar.<sup>14</sup> This model is

also substantiated by the observation of apparently completely equivalent  $\beta$ -hydrogen atoms for the alcohol adducts in the cyclic form. Thus, this can only happen if interconversion occurs between two conformations with equivalent sets of splittings [*i.e.* ring flipping of (18)] and if the two conformations have similar energies (contrast, for instance, the situation with 4-alkylpiperidyl nitroxides<sup>21</sup>). The latter requirement may seem at first surprising, especially as the effect is observed for fairly large substituents R (*e.g.* R = Me, Et, Pr, or Ph); however inspection of models makes it quite clear that the substituent R in these examples should not have any



clear preference for the pseudo-axial or -equatorial positions, unlike cyclohexane derivatives. Thus the four atoms of the ring comprising the nitroxide and hydroxy-groups have no substituents which would provide unfavourable steric interaction with an alkyl group (R) in the axial position.

*Conclusions.*—We have shown how a recognition of chiral effects in e.s.r. spectra can be a useful aid for radical recognition and how some interesting conformational aspects can be elucidated. We are currently engaged in an extension of the investigation of solvent and temperature effects, further to investigate the consequences of an asymmetric centre in a radical on the resulting e.s.r. spectra.

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