J. Chem. Soc., Faraday Trans. 1, 1983, **79**, 439-452

Rotational Correlation Times and Radii of Dithiazol-2-yl and Dithiazolidin-2-yl Free Radicals

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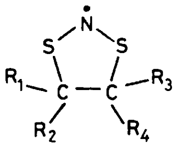
Received 23*rd April*, 1982

1,3,2-Dithiazol-2-yl and 1,3,2-dithiazolidin-2-yl radicals have been shown to be useful model compounds for detailed e.s.r. studies of rotational reorientation in liquid and frozen media. Consequently they are also potentially useful spin probes and spin labels. The e.s.r. powder spectra have been analysed and the resulting *g* and *A* tensors were used to calculate rotational diffusion coreslation times, rotational energetics of activation and effective radii. The latter are a closer match to radii calculated from geometric radii than has been found for model nitroxy radicals: the energetics of activation for rotational diffusion indicate that the non-polar character of our radicals minimises solute–solvent interactions.

In a previous paper[1] from this laboratory we showed that a variety of persistent free radicals can be formed by low-temperature thermal reactions of tetrasulphur dinitride with strained alkenes. The radicals are believed[1, 2] to be derivatives of the novel 1,3,2-dithiazolidine heterocycles (**1**) where R_1 and R_3 are usually the 2 and 3 carbon atoms of a norbornyl fragment while R_2 and R_4 are usually the hydrogen atoms in the *endo* positions. Recently we have found[3] that tetrasulphur dinitride also reacts thermally with alkynes to give long-lived free radicals having the unusual 1,3,2-dithiazol-2-yl structure (**2**) where R_1 and R_2 can be aromatic, alkyl, fluoroalkyl, amide or ester groups (see fig. 1).



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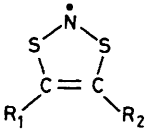

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The e.s.r. spectra of both types of radicals resemble nitroxides in that their powder spectra show approximate axial symmetry and they have a large nitrogen anisotropy which manifests itself in the marked asymmetric line-broadening for viscous solutions. [See ref. (1) for examples of line broadening in the spectra of dithiazolidin-2-yl radicals.] This present paper describes how we have used the effect to calculate the dimensions of both classes of radicals. Also we have been able to measure the energetics of activation for rotational diffusion. The radicals are good models for testing theoretical

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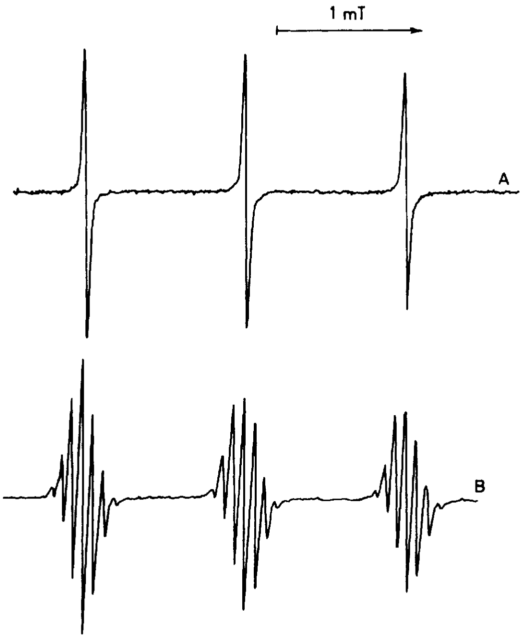


FIG. 1.—First-derivative X-band e.s.r. spectra of (A) the radical from dimethylacetylene dicarboxylate and S_4N_2 in $CHCl_3$ at +22 °C, (B) the radical from hexafluorobut-2-yne and S_4N_2 in $CFCl_3$ at −35 °C.

treatments because of their rigidity. Additionally, they are potentially useful spin probes and spin labels which can be prepared easily with nitrogen-14 replaced by nitrogen-15.[4]

EXPERIMENTAL

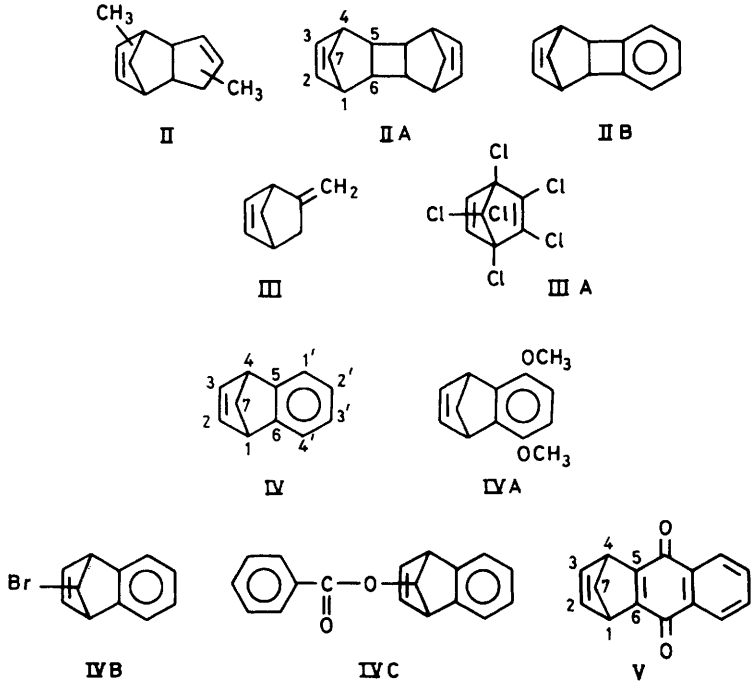
MATERIALS

Norbornene (bicyclo[2.2.1]-hept-2-ene) (I), 5-methyl-norborn-2-ene (I A), 5-cyanonorborn-2-ene (I B), 5-acetoxynorborn-2-ene (I C), methylcyclopentadiene dimer (II) and dinorborn-2-ene (pentacyclo[8.2.$1.^{4,7}0^{2,9}.0^{3,8}$]-tetradeca-5,11-diene) (II A) were purchased from Aldrich Chemicals. *endo*-3,4-Benzotricyclo[4.2.$10^{2,5}$]nona-3,7-diene (II B) was donated by Prof. R. Baker of Southampton University. 5-Methylene-norborn-2-ene (III) and 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-hepta-2,5-diene (III A) were bought from Aldrich Chemicals: the latter compound was supplied under water and was dried with magnesium sulphate. Benzonorbornadiene (IV) was given to us by Prof. S. Trahanovsky of Iowa State University and 1′,4′-dimethoxybenzonorbornadiene (IV A) was kindly provided by Prof. N. Filipescu of George Washington University. 7-*syn*-Bromobenzonorbornadiene (IV B) and benzonorbornadiene-7-*syn*-benzoate (IV C) were both gifts from Prof. J. W. Wilt of Loyola University of Chicago. Norbornadienenaphthaquinone (V) was generously provided by Prof. L. A. Paquette of Ohio State University. The structures of some of these norbornenes are shown in table 1.

Diphenylacetylene, dimethylacetylene dicarboxylate and perdeuterotoluene were supplied by Aldrich Chemicals, while hexafluorobut-2-yne came from Fluorochem Ltd. Methylphenylacetylene was a gift from Mr J. Crabb.

Large-scale (*ca.* 1 g) preparations of tetrasulphur dinitride were made[5] by the reaction of tetrasulphur tetranitride with sulphur. For most experiments it was not necessary to separate the product from the reactants. The product was more stable when stored in a solvent, *e.g.* carbon tetrachloride.[6] Small amounts of tetrasulphur dinitride (*ca.* 1 mg) were obtained[7] by treating a solution of disulphur dibromide or of disulphur dichloride in carbon tetrachloride

TABLE 1.—SOME ALKENES USED TO PREPARED DITHIAZOLIDIN-2-YL RADICALS



with ammonia gas until a pH of 8 resulted: again the product is a mixture of tetrasulphur dinitride, tetrasulphur tetranitride and sulphur. Solutions of tetrasulphur dinitride free from tetrasulphur tetranitride were prepared by the chromatographic method reported by Adkins and Turner.[8] Tetrasulphur tetranitride labelled with nitrogen-15 was prepared on the milligram scale using ammonia containing 98.6 atom % nitrogen-15: the latter was supplied by Oriel Scientific Ltd.

E.S.R. MEASUREMENTS

A Varian E-4 e.s.r. spectrometer was used to obtain the spectra. Details of sample preparation, spectrometer calibration, *g*-factor measurements, computer simulations and temperature measurements have been given previously.[1, 9]

The spectra of solutions and of frozen glasses of the radicals were recorded for a range of temperatures: the lowest temperature used for glasses was −155 °C in an attempt to reach the powder spectrum rigid limit. Perdeuterotoluene was used in some of the experiments to give better resolution.[10] Solid diphenylpicrylhydrazyl was used as a *g*-factor reference for the powder spectra. The latter were simulated using a computer program written by Dr C. F. Polnaszek[11] and adapted to run on the Liverpool University ICL 1906S computer by Miss S. M. Taylor.

RESULTS AND DISCUSSION

The widths of e.s.r. lines and variations in widths can be accounted for by the motional modulation of the *g*-factor and hyperfine (*A*) tensors of a free radical. The effects can be treated as perturbations of the time-independent spin Hamiltonian, and, since the lines are Lorentzian, a complete line-shape analysis is not necessary. Line-width measurements are sufficient to determine the rate of tumbling providing that the anisotropic g and A tensors are known and that the rate of tumbling is fast (2×10^{10} to $5\times10^{8}\ \mathrm{s}^{-1}$). McConnell[12] has derived the following expression for linewidths:[13-19]

$$[T_2(m_I)]^{-1} = A + Bm_I + Cm_I^2$$

where m_I is the nuclear magnetic quantum number and A, B and C are functions of the g and A tensors and of the rotational correlation times, τ_c. For our radicals containing nitrogen-14, the low- and high-field lines correspond to m_I values of $+1$ and -1, respectively, because the isotropic coupling constant, $a^{N^{14}}$, is positive.[9] Thus the difference in width of these two lines gives the value of B:

$$[T_2(-1)]^{-1} - [T_2(+1)]^{-1} = -2B.$$

Since it is easier to measure line heights (h) rather than widths and because the peak-to-peak height of the first derivative of a Lorentzian line varies as the inverse square of the line width, B can be determined from the relationship

$$B = \frac{\sqrt{3}[W(+1)]}{4}\left[1-\left(\frac{h(+1)}{h(-1)}\right)^{\frac{1}{2}}\right]$$

where $W = 2(\sqrt{3}T_2)^{-1}$ for the peak-to-peak width of a first-derivative Lorentzian line shape.

The rotational correlation time can be calculated from values of B using the expression

$$B = \tfrac{4}{15} b \Delta B_0 \tau_c$$

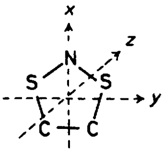
where

$$b = 4\pi[A_{zz} - (A_{xx} + A_{yy})/2]/3$$

$$\Delta = \beta_e \hbar^{-1}[g_{zz} - (g_{xx} + g_{yy})/2]$$

and B_0 is the operating field of the spectrometer.

In applying these expressions it is assumed that the axes for the g and A tensors are coincident. Ondar *et al.*[20] have shown recently, from powder spectra recorded with a 2 mm wavelength spectrometer having a superconducting magnet, that this assumption is valid for a range of nitroxides. For our radicals the axes are defined as follows:



The values of A_{zz} determined from the powder spectra are large compared with A_{xx} and A_{yy}, which are probably equal (see table 2). This means that the A tensors can be regarded as being essentially axially symmetric. Thus most of the unpaired spin density is located on the nitrogen atom in a p orbital approximately at right angles to the heterocyclic ring. The anisotropic parameters for our radicals are similar to those measured for nitroxides.[19] The signs of the anisotropic coupling constants are expected to be the same[21] because of the large positive value of $a^{N^{14}}$. Following Symons and Smith[21] we have verified the equality of the signs by observing that A_{zz} (as measured from the extrema of the powder spectrum) increases as the temperature is decreased (see table 3).

The correlation times measured from B values can be in error if the radical is undergoing anisotropic motion.[22] There is some evidence that this is happening with our radicals in that in most cases the low-field line is slightly sharper than the mid-field

TABLE 2.—ANISOTROPIC g^a AND A^b TENSORS OF DITHIAZOL-2-YL RADICALS AT RIGID LIMIT

Radical from PhC≡CPh in perdeuterotoluene at −145 °C:

g_{xx}	g_{yy}	g_{zz}	A_{xx}^{N14}	A_{yy}^{N14}	A_{zz}^{N14}
2.0140	2.0048	2.0021	+0.23	+0.23	+2.77

Radical from PhC≡CPh labelled with 99 atom % nitrogen-15 in carbon tetrachloride at −145 °C:

g_{xx}	g_{yy}	g_{zz}	A_{xx}^{N15}	A_{yy}^{N15}	A_{zz}^{N15}
2.0130	2.0040	2.0020	−0.28	−0.28	−3.92

[a] Errors are estimated to be ±0.0002; [b] in mT.

TABLE 3.—TEMPERATURE DEPENDENCE OF A_{zz} FROM POWDER SPECTRA OF DITHIAZOL-2-YL RADICALS

alkyne (matrix)	T/°C	A_{zz}^{N14}/mT	T/°C	A_{zz}^{N15}/mT
PhC≡CPh (solid)	−1.0	+2.750	−40.0	−4.025
	−41.5	+2.768	−89.1	−4.150
	−72.5	+2.765	−145.5	−4.287
	−101.0	+2.783		
	−131.0	+2.800		
	−155.0	+2.808		
PhC≡CPh[a] (CCl_4)	−61.7	+2.756	−144.0	−4.175
	−79.5	+2.768	−149.0	−4.213
	−115.0	+2.788		
	−130.0	+2.773		
	−145.0	+2.788		

[a] Solution spectra at 21.7 °C gave values for a^{N14} and a^{N15} of 1.075±0.006 mT and 1.502±0.003 mT.

line. Whether the effect is significant can be checked by calculating the correlation times as measured both from B and from C (τ_c^B and τ_c^C): if the two results agree then anisotropic motion is unimportant. The value of C can be determined from the line widths of all three lines using the expression

$$C = \frac{\sqrt{3}[W(0)]}{4}\left[\left(\frac{h(0)}{h(+1)}\right)^{\frac{1}{2}} + \left(\frac{h(0)}{h(-1)}\right)^{\frac{1}{2}} - 2\right]$$

where $C = b^2\tau_c/8$.

The parameter B was evaluated from solution spectra of nitrogen-15 labelled radicals using the expression

$$B = [T_2(+\tfrac{1}{2})]^{-1} - [T_2(-\tfrac{1}{2})]^{-1}$$

or, in terms of peak heights and widths,

$$B = \frac{\sqrt{3}}{2}[W(-\tfrac{1}{2})]\left[\left(\frac{h(-\frac{1}{2})}{h(+\frac{1}{2})}\right)^{\frac{1}{2}} - 1\right].$$

The magnetogyric ratio of nitrogen-15 is negative hence the coupling constants are negative, which means that the low-field line has $m_I = -\frac{1}{2}$. Unfortunately it is not possible to calculate C from the nitrogen-15 spectra.

Poggi and Johnson[23] have reviewed the errors likely to be encountered in the evaluation of τ_c using the above treatment. The most important of these is that arising from the use of line heights as a measure of line widths when extra hyperfine coupling (resolved or unresolved) are present. Such coupling causes the line shapes to depart from Lorentzian.

DITHIAZOL-2-YL RADICALS

Since it is possible to obtain these radicals with no coupling other than that from the nitrogen nucleus they provide excellent models with which to test tumbling theory: the radicals have low-field line widths of *ca.* 0.02 mT. Furthermore, their chemical properties make them potentially useful spin probes and spin labels. Consequently, we have analysed in detail the powder spectrum of the radical prepared from diphenyl acetylene with nitrogen-14 or substituted with nitrogen-15. Fig. 2 and 3 show these spectra along with the computed spectra: the spectral parameters used for the computations are listed in table 2. Note that line widths of 0.2-0.3 mT were used in the spectral simulations hence it was not possible to detect any differences between A_{xx} and A_{yy}. Although the isotropic *g*-factor value of 2.0065 is similar to that for nitroxy radicals the anisotropic values do show differences.

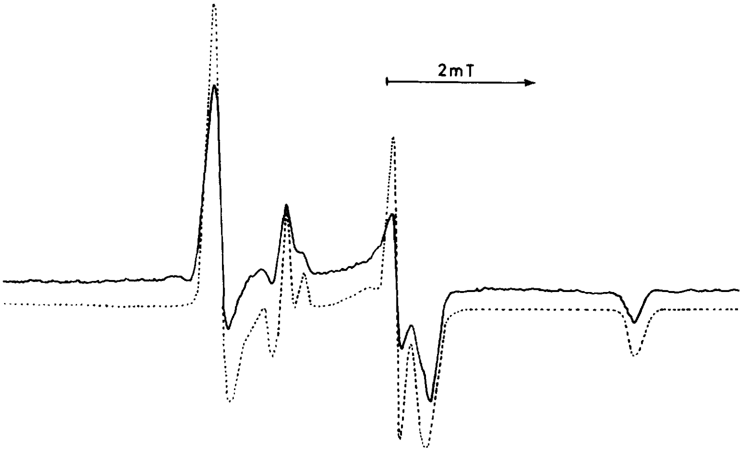


FIG. 2.—First-derivative X-band e.s.r. powder spectrum at −145 °C of the radical formed from diphenylacetylene and S_4N_2 in perdeuterotoluene. The full line is the experimental spectrum while the dotted line is a computer simulation from the parameters listed in table 2 and a line width of 0.1 mT.

We have recorded the liquid e.s.r. spectra of a variety of radicals in different solvents over a range of temperatures. From the spectra we measured the line-height ratios for each spectrum. Tables 4-6 list some of the data obtained. For the nitrogen-14 radicals we calculated τ_c from both *B* and *C* and it can be seen that the differences are small, thus confirming that the rotational diffusion is essentially isotropic. There is also reasonable agreement between these values of τ_c and those derived from the nitrogen-15 spectra. From the temperature dependence of τ_c we have calculated the energetics of activation for radical tumbling. From table 7 it can be seen that the barriers to rotational diffusion are not greatly affected by radical type or by solvent. These results show that the dithiazolyl radicals provide excellent models.

The radical containing trifluoromethyl groups does have a smaller barrier to rotation than the others: we have not been able to prepare a radical from but-2-yne itself.

According to the Debye diffusion model[24] the correlation time for rotational diffusion is given by[25]

$$\tau_c = 4\eta\pi r^3/3kT$$

where η is the solvent viscosity, k Boltzmann's constant, T the absolute temperature and r the effective radius of the molecule. After calculating η, for the temperatures used in this work, from the expression

$$\log_{10}\eta = \frac{B}{T}+C$$

(taking values of viscosities from standard tables) we obtained the values of r^B and r^C given in table 7.

It may be seen that values of τ_c are smaller when carbon tetrachloride is the solvent compared with methanol. Windle[26] found a similar result for τ_c values of nitroxy radicals in carbon tetrachloride and in water. We have estimated[3] the dimensions of the heterocycle part of the structure of the dithiazolyl radicals from INDO calculations of the unpaired spin-density distribution. From these results we have calculated the radii about the x, y and z axes (listed in table 7). Also we have calculated the spherical equivalent radius from the expression

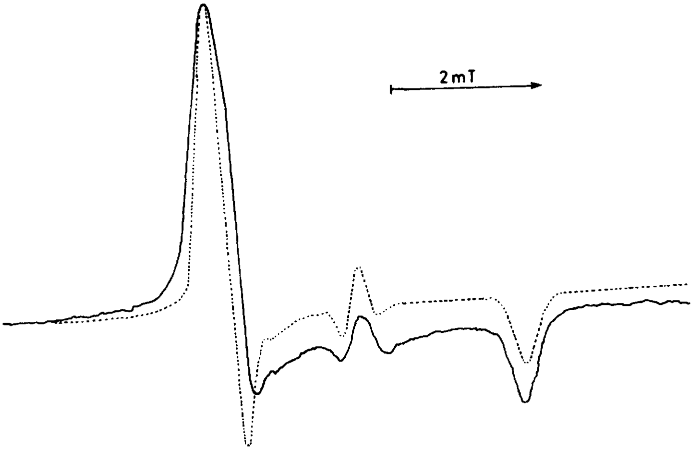


FIG. 3.—The first-derivative X-band e.s.r. powder spectrum at −145 °C of the radical formed from diphenylacetylene and S_4N_2 labelled with 99 atom % nitrogen-15 in carbon tetrachloride. The full line is the experimental spectrum while the dotted line is a computer simulation from the parameters listed in table 2 and a line width of 0.2 mT.

$$r_s = (r_x r_y r_z)^{\frac{1}{3}}.$$

It can be seen from table 7 that there is good agreement between the values of the effective radii calculated from both B and C. Because of the limited number of substituted alkynes we have investigated so far a wide range of radii have not been encountered. However, the fluorinated radical is much smaller than the others, and this is reflected also in the lower barrier to rotational diffusion. As is usually found in this type of work the values of radii obtained are smaller than expected from structural considerations.[26] In general, the consistency in the r values was lost when τ_c became $> 10^{-10}$ s.

TABLE 4.—ROTATIONAL CORRELATION TIMES AND RADII OF DITHIAZOL-2-YL RADICALS MADE FROM 1,4-DIPHENYLBUTYNE-2

solvent	T/K	viscosity /kg m^{-1} s^{-1}	$h(+1)$ /mm	$h(0)$ /mm	$h(-1)$ /mm	$W(+1)$ /mT	B/mT	C/mT	τ_c^B/s	τ_c^C/s	r^B/nm	r^C/nm
CCl_4	328.0	6.14×10^{-4}	181.0	169.8	130.3	0.0286	-2.21×10^{-3}	1.39×10^{-3}	4.05×10^{-12}	3.23×10^{-12}	0.192	0.178
	311.1	7.55×10^{-4}	209.4	199.0	145.2	0.0296	-2.53×10^{-3}	1.91×10^{-3}	4.71×10^{-12}	4.44×10^{-12}	0.186	0.182
	291.1	9.96×10^{-4}	204.2	196.0	127.8	0.0266	-3.03×10^{-3}	2.55×10^{-3}	5.60×10^{-12}	5.93×10^{-12}	0.175	0.178
	277.0	1.24×10^{-3}	233.8	226.2	137.5	0.0271	-3.56×10^{-3}	3.14×10^{-3}	6.56×10^{-12}	7.31×10^{-12}	0.169	0.175
	263.9	1.55×10^{-3}	223.2	216.4	107.8	0.0275	-5.15×10^{-3}	5.15×10^{-3}	9.46×10^{-12}	1.19×10^{-11}	0.174	0.189
	253.2	1.90×10^{-3}	208.2	202.6	88.8	0.0292	-6.73×10^{-3}	6.34×10^{-3}	1.25×10^{-11}	1.41×10^{-11}	0.176	0.186
	241.8	2.39×10^{-3}	225.9	213.2	76.5	0.0320	-9.95×10^{-3}	9.12×10^{-3}	1.83×10^{-11}	2.12×10^{-11}	0.183	0.192
n-C_6H_{14}	294.0	3.25×10^{-4}	238.3	237.5	234.2	0.0282	-1.23×10^{-3}	6.70×10^{-4}	2.26×10^{-12}	1.55×10^{-12}	0.189	0.167
	253.0	5.14×10^{-4}	221.8	210.0	173.5	0.0289	-1.63×10^{-3}	9.40×10^{-4}	3.01×10^{-12}	2.18×10^{-12}	0.169	0.152
	201.5	9.74×10^{-4}	231.2	222.2	160.6	0.0320	-2.78×10^{-3}	2.21×10^{-3}	5.10×10^{-12}	5.13×10^{-12}	0.152	0.152
	183.9	1.76×10^{-3}	210.5	199.5	102.5	0.0317	-5.95×10^{-3}	5.21×10^{-3}	1.09×10^{-11}	1.21×10^{-11}	0.156	0.161

TABLE 5.—ROTATIONAL CORRELATION TIMES AND RADII OF DITHIAZOL-2-YL RADICALS

alkyne (solvent)	T/K	viscosity /kg m^{-1} s^{-1}	B/mT	C/mT	$\tau_c{}^B$/s	$\tau_c{}^C$/s	r^B/nm	r^C/nm
$CF_3C{\equiv}CCF_3$[a]	228.0	9.12×10^{-4}	-5.82×10^{-4}	3.17×10^{-4}	1.07×10^{-12}	7.36×10^{-13}	0.096	0.085
(CH_2Cl_2)	207.0	1.29×10^{-3}	-1.14×10^{-4}	5.43×10^{-4}	1.31×10^{-12}	1.26×10^{-12}	0.089	0.087
	188.0	1.88×10^{-3}	-1.63×10^{-3}	1.14×10^{-3}	3.00×10^{-12}	2.65×10^{-12}	0.100	0.096
	170.0	2.91×10^{-3}	-3.03×10^{-3}	2.14×10^{-3}	5.57×10^{-12}	4.99×10^{-12}	0.102	0.098
$MeOOCC{\equiv}CCOOMe$	294.7	5.86×10^{-4}	-1.74×10^{-3}	1.03×10^{-3}	3.20×10^{-12}	2.38×10^{-12}	0.174	0.158
($CHCl_3$)	253.0	9.35×10^{-4}	-3.20×10^{-3}	2.20×10^{-3}	5.87×10^{-12}	5.10×10^{-12}	0.174	0.166
	213.0	1.74×10^{-3}	-6.86×10^{-3}	5.71×10^{-3}	1.26×10^{-11}	1.32×10^{-11}	0.172	0.174
$PhC{\equiv}CMe$	294.7	3.20×10^{-4}	-5.95×10^{-4}	5.76×10^{-4}	1.09×10^{-12}	1.34×10^{-12}	0.149	0.160
(n-C_6H_{14})	253.0	5.14×10^{-4}	-2.38×10^{-3}	1.41×10^{-3}	4.39×10^{-12}	3.28×10^{-12}	0.192	0.174
	207.5	1.05×10^{-3}	-4.41×10^{-3}	4.27×10^{-3}	8.10×10^{-12}	9.92×10^{-12}	0.174	0.186
$PhC{\equiv}C{-}C{\equiv}CPh$	311.0	4.67×10^{-4}	-1.63×10^{-3}	7.91×10^{-4}	3.01×10^{-12}	1.84×10^{-12}	0.187	0.159
(CH_3OH containing	294.0	5.88×10^{-4}	-2.18×10^{-3}	1.34×10^{-3}	4.00×10^{-12}	3.12×10^{-12}	0.187	0.173
10^{-5} mol dm^{-3} KOH)	214.0	2.90×10^{-3}	-1.33×10^{-2}	9.62×10^{-3}	2.43×10^{-11}	2.23×10^{-11}	0.181	0.176
	187.9	7.37×10^{-3}	-3.94×10^{-2}	2.87×10^{-2}	7.25×10^{-11}	6.62×10^{-11}	0.183	0.177

[a] B and C values were calculated from intensities of central lines of septets.

TABLE 6.—ROTATIONAL CORRELATION TIMES AND RADII OF DITHIAZOL-2-YL RADICALS SUBSTITUTED WITH 99 ATOM % NITROGEN-15

alkyne (solvent)	T/K	viscosity /kg m^{-1} s^{-1}	B/mT	τ_c/s	r/nm
MeOOCC≡CCOOMe	428.0	4.8×10^{-4}	1.03×10^{-3}	1.23×10^{-12}	0.154
($C_6H_5OCH_3$)	373.0	6.75×10^{-4}	1.79×10^{-3}	2.13×10^{-12}	0.158
	333.0	9.27×10^{-4}	3.09×10^{-3}	4.38×10^{-12}	0.173
	298.0	1.31×10^{-3}	3.06×10^{-3}	3.64×10^{-12}	0.140
	291.0	1.42×10^{-3}	3.86×10^{-3}	4.58×10^{-12}	0.146
MeOOCC≡CCOOMe	293.1	4.28×10^{-4}	2.02×10^{-3}	2.40×10^{-12}	0.175
(CH_2Cl_2)	273.0	5.21×10^{-4}	1.99×10^{-3}	2.37×10^{-12}	0.160
	252.0	6.60×10^{-4}	2.70×10^{-3}	3.23×10^{-12}	0.161
	213.0	1.16×10^{-3}	5.24×10^{-3}	6.73×10^{-12}	0.156
	193.0	1.69×10^{-3}	1.09×10^{-2}	1.32×10^{-11}	0.170
PhC≡CPh	295.1	5.79×10^{-4}	3.39×10^{-3}	4.02×10^{-12}	0.189
(CH_3OH containing	253.0	1.17×10^{-3}	6.89×10^{-3}	8.21×10^{-12}	0.180
10^{-5} mol dm^{-3} KOH)	212.5	3.02×10^{-3}	1.67×10^{-2}	1.98×10^{-11}	0.166
	183.9	8.85×10^{-3}	5.10×10^{-2}	6.06×10^{-11}	0.160
$CF_3C{\equiv}CCF_3$^{a} (CCl_4)	283.9	1.11×10^{-3}	6.64×10^{-4}	7.91×10^{-12}	0.087
	264.9	1.52×10^{-3}	1.24×10^{-3}	1.47×10^{-12}	0.094
	251.9	1.94×10^{-3}	1.64×10^{-3}	1.95×10^{-12}	0.094
	243.6	2.30×10^{-3}	2.57×10^{-3}	3.06×10^{-11}	0.102
	233.4	2.88×10^{-3}	3.50×10^{-3}	4.16×10^{-11}	0.104

[a] B values calculated from intensities of central lines of septets.

DITHIAZOLIDIN-2-YL RADICALS

All these radicals have large proton couplings from R_2 and R_4 and there are also other couplings, resolved and unresolved, from other parts of the 2,2,1-bicycloheptyl (norbornyl) fragment.[1] Consequently, we have not undertaken a detailed analysis of the powder spectra (fig. 4 and 5) of the nitrogen-14 and nitrogen-15 radicals. The radical prepared from dimethoxybenzonorbornadiene and S_4N_2 was used for this part of the work because the solution spectra have narrow lines.[9] Measurements from the extrema of the powder spectra gave values for A_{zz} and g_{zz} and, from these, average values of A_{xx} and A_{yy} and of g_{xx} and g_{yy} were determined (table 8) using the relationships

$$(A_{xx}+A_{yy})/2 = (3a-A_{zz})/2$$

$$(g_{xx}+g_{yy})/2 = (3g_{\text{iso}}-g_{zz})/2.$$

From the experimental data given in table 8 we get

$$(A_{xx}^{\text{N14}}+A_{yy}^{\text{N14}})/2 = 0.364\ \text{mT}$$

$$(A_{xx}^{\text{N15}}+A_{yy}^{\text{N15}})/2 = -0.396\ \text{mT}$$

$$(g_{xx}+g_{yy})/2 = 2.0087.$$

The A^{N14} and A^{N15} values differ by a factor other than that calculated from the magnetogyric ratios due to non-reproducibility of the powder matrix. The results given in table 9 for a wide variety of dithiazolidinyl radicals were calculated using these values. The radicals labelled with 99 atom % nitrogen-15 give rigid limit e.s.r. spectra

TABLE 7.—ENERGETICS[a] OF ROTATIONAL DIFFUSION AND EXPERIMENTAL AND CALCULATED RADII OF DITHIAZOL-2-YL RADICALS

alkyne	solvent	r^B/nm	r^C/nm	r_x/nm	r_y/nm	r_z/nm	r_s/nm	ΔG^*_{298} /kJ mol^{-1}	ΔH^*_{298} /kJ mol^{-1}	ΔS^*_{298} /J mol^{-1} K^{-1}
PhC≡CPh	CCl_4	0.180±0.008	0.183±0.006	0.41	0.35	0.41	0.39	12.5±1.1	8.6±0.8	5±5
	n-C_6H_{14}	0.167±0.017	0.158±0.007					10.9±1.5	4.9±0.7	−20±3
	CH_3OH	0.174±0.014[b]	—					11.4±0.7	8.4±0.5	−10±2
MeOOCC≡CCOOMe	$CHCl_3$	0.173±0.013	0.166±0.008	0.49	0.26	0.49	0.40	10.8±0.2	6.3±0.1	−15±1
	$C_6H_5OCH_3$	0.154±0.012[b]	—					11.9±4.5	6.8±2.4	−17±7
	CH_2Cl_2	0.165±0.008[b]	—					9.8±1.5	5.6±0.9	−14±3
$CF_3C≡CCF_3$	CH_2Cl_2	0.096±0.006[b]	0.092±0.007	0.28	0.24	0.28	0.27	4.9±1.0	7.3±1.3	8±6
	CCl_4	0.096±0.007	—					6.8±0.5	15.7±1.0	30±4
PhC≡CMe	n-C_6H_{14}	0.172±0.021	0.173±0.014	0.35	0.35	0.34	0.35	8.8±1.6	9.4±1.8	2±8
PhC≡C—C≡CPh	CH_3OH	0.185±0.003	0.171±0.008	0.44	0.44	0.44	0.44	11.5±0.3	10.0±0.3	−5±1

[a] Obtained from $(\tau_C^B)^{-1}$; [b] obtained from radicals labelled with 99 atom % nitrogen-15.

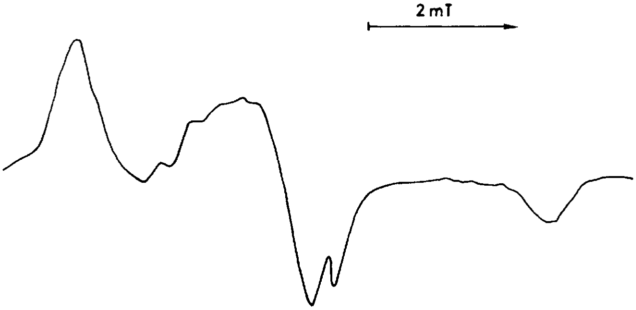


FIG. 4.—First-derivative X-band e.s.r. powder spectrum at −145 °C of the solid radical formed from 1′,4′-dimethoxybenzonorbornadiene and S_4N_2.

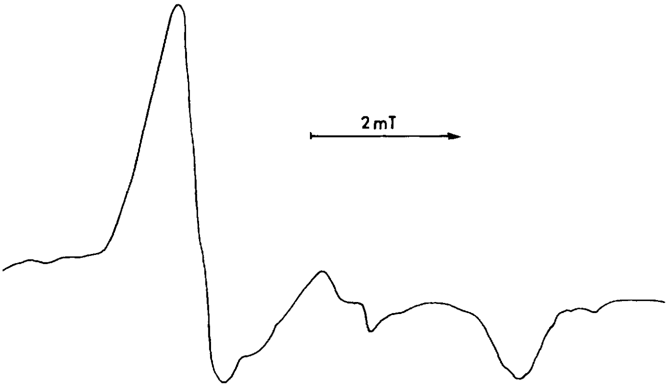


FIG. 5.—First-derivative X-band e.s.r. powder spectrum at −145 °C of the solid radical formed from 1′,4′-dimethoxybenzonorbornadiene and S_4N_2 labelled with 99 atom % nitrogen-15.

TABLE 8.—E.S.R. SPECTRAL PARAMETERS FOR THE DITHIAZOLIDIN-2-YL RADICAL FORMED FROM 1′,4′-DIMETHOXYBENZONORBORNADIENE

a^{N14} = +1.305 mT (CCl_4 at 22 °C)
A_{zz}^{N14} = +3.188 mT (solid radical)
a^{N15} = −1.825 mT (CH_2Cl_2 at 20 °C)
A_{zz}^{N15} = −4.638 mT (solid radical)
g_{iso} = 2.006 50
g_{zz} = 2.0021

(fig. 5) which are similar to that reported[4] for the nitroxide TEMPOL substituted with nitrogen-15. Because of the more complicated e.s.r. spectra involved we only used parameter B to calculate τ_c and subsequently r. For the sake of brevity, data from only two representative temperatures are listed. From the temperature dependence of τ_c the energetics of activation were calculated (table 9). The entropy of activation is expected to be near zero hence departures from this value are likely to arise from experimental errors. The free energy of activation is relatively independent of the nature of the substituents and the size of the radical. Although the effective radii of the radical are certain to be too small they do parallel the size of the substituents: it is surprising, however, that the radical made from 5-acetoxynorbornene appears to be one of the larger radicals. As found for the dithiazolyl radicals the values of τ_c

TABLE 9.—CORRELATION TIMES, ROTATIONAL ACTIVATION ENERGETICS AND RADII OF DITHIAZOLIDIN-2-YL RADICALS

alkene	solvent	T/K	$h(+1)$ /$h(-1)$	$W(+1)$ /mT	B/mT	τ_c/s	r/nm	ΔH^*_{293} /kJ mol^{-1}	ΔG^*_{293} /kJ mol^{-1}	ΔS^*_{293} /J mol^{-1} K^{-1}
norbornene(I)	CH_2Cl_2	293	1.15	0.05	-1.57×10^{-3}	2.65×10^{-12}	0.181	5.8	9.9	−14
		213	1.39		−3.88	6.56×10^{-12}	0.159			
5-methylnorbornene(IA)	CH_2Cl_2	293	1.15	0.05	−1.57	2.65×10^{-12}	0.181	7.2	9.9	−9
		213	1.49		−4.77	8.05×10^{-12}	0.170			
5-cyanonorbornene(IB)	CH_2Cl_2	293	1.19	0.05	−1.97	3.31×10^{-12}	0.196	8.8	10.5	−6
		213	1.84		−7.72	1.30×10^{-11}	0.199			
5-acetoxynorbornene(IC)	CH_2Cl_2	293	1.29	0.05	−2.94	4.96×10^{-12}	0.224	13.9	11.4	+8
		223	3.29		−17.62	2.97×10^{-11}	0.236			
methylcyclopentadiene(II)	CH_2Cl_2	303	1.08	0.05	−0.85	1.44×10^{-12}	0.161	6.0	8.8	−9
		213	1.79		−7.31	1.23×10^{-11}	0.196			
dinorbornene(IIA)	i-C_5H_{12}	293	1.08	0.05	−0.85	1.44×10^{-12}	0.191	10.3	8.4	+6
		213	1.42		−4.16	7.03×10^{-12}	0.198			
dinorbornene(IIB)	i-C_5H_{12}	303	1.24	0.05	−2.26	4.16×10^{-12}	0.208	5.5	11.5	−20
		213	1.60		−5.73	9.70×10^{-12}	0.221			
5-methylenenorbornene(III)	CH_2Cl_2	253	1.27	0.05	−2.73	4.63×10^{-12}	0.181	2.8	9.4	−26
		213	1.42		−4.16	7.03×10^{-12}	0.154			
hexachloronorbornene(IIIA)	CH_2Cl_2	293	1.22	0.05	−2.26	3.83×10^{-12}	0.206	12.1	10.8	+4
		213	2.80		−14.58	2.46×10^{-11}	0.247			
benzonorbornadiene(IV)	CH_2Cl_2	293	1.23	0.035	−1.65	2.78×10^{-12}	0.185	9.3	10.0	−3
		213	2.13		−6.93	1.38×10^{-11}	0.193			
1′,4′-dimethoxybenzo-norbornadiene(IVA)	CH_2Cl_2	293	1.35	0.017	−1.19	2.01×10^{-12}	0.165	5.8	9.2	−12
		213	1.95		−2.92	4.93×10^{-12}	0.151			
^{15}N-1′,4′-dimethoxybenzo-norbornadiene(IVA)	CH_2Cl_2	293	1.56[a]	0.017[b]	+1.85	2.05×10^{-12}	0.167	5.4	9.3	−13
		213	3.34[a]		+6.09	6.84×10^{-12}	0.161			
7-*syn*-bromobenzo-norbornadiene(IVB)	CH_2Cl_2	293	1.33	0.02	−1.33	2.24×10^{-12}	0.172	13.3	9.5	+13
		213	4.80		−10.31	1.74×10^{-11}	0.219			
7-*syn*-benzoatebenzo-norbornadiene(IVC)	CH_2Cl_2	293	2.09	0.02	−3.86	6.53×10^{-12}	0.245	6.5	12.1	−19
		213	4.90		−10.50	17.75×10^{-12}	0.221			
norbornadiene naphthaquinone(V)	CH_2Cl_2	293	1.33	0.02	−1.33	2.24×10^{-12}	0.172	13.2	9.5	+13
		213	4.69		−10.09	17.06×10^{-12}	0.218			

[a] $h(-\frac{1}{2})/h(+\frac{1}{2})$. [b] $W(-\frac{1}{2})$.

and r are not significantly dependent on solvent type. The dithiazolidinyl radicals may be less useful as model compounds than the dithiazolyl radicals but the hyperfine coupling from two hydrogen nuclei of the norbornyl ring can be reduced from *ca.* 0.3 mT to 0.05 mT by deuteration.[3]

CONCLUSIONS

In the past both perdeutero-2,2,6,6-tetramethyl-4-piperidone *N*-oxide and peroxylaminedisulphonate radicals have been used[10, 27, 28] as model compounds for relaxation studies of rotational reorientation in liquid and frozen media. This paper shows that the dithiazol-2-yl and dithiazolidin-2-yl radicals we have discovered provide better model compounds. Both types of radicals have rigid structures and both can be prepared easily with nitrogen-15 in place of nitrogen-14. The dithiazol-2-yl radicals have line widths as small as those of peroxylaminedisulphonate while the deuterated radical formed from perdeuteronorbornene is simple to prepare.[2, 3]

Our radicals are non-polar hence we have been able to achieve a greater precision in the determination of effective rotational radii than Freed *et al.*[27] found possible for nitroxy radicals: the elaborate procedure used for calculating the geometric radii is no more successful than our simple one of calculating the equivalent spherical radii.

We express our gratitude to Miss S. M. Taylor for carrying out all the computations of powder spectra. We also thank the S.E.R.C. for providing a research assistantship for S.A.F. and a maintenance grant for R.S.P.

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