

Structure of Pentafluorobenzaldehyde determined from Nuclear Magnetic Resonance Spectra of Nematic Solutions

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Dipolar coupling constants obtained from an analysis of the n.m.r. spectrum of pentafluorobenzaldehyde dissolved in the nematogen Merck Phase IV have been compared with various models of the equilibrium structure. A normal co-ordinate calculation has been carried out for pentafluorobenzaldehyde in order to allow for vibrational averaging of dipolar couplings. It is concluded that the equilibrium structure is planar with a high barrier to internal rotation of the formyl group.

DIPOLAR couplings, D_{ij} , obtained from the analysis of the n.m.r. spectrum of a molecule dissolved in a nematic mesophase, are averages over any internal motion faster than D_{ij}^{-1} , and can be used therefore to test models of internal rotation. Previous examples studied by this method have usually given satisfactory agreement with other structural methods; thus in the case of benzaldehyde¹ the n.m.r. data are consistent with equilibrium structures which have all the protons coplanar. The structure of pentafluorobenzaldehyde is not known, and the aim of the present study is to discover the extent of the information that can be obtained about the equilibrium structure, and the barrier to internal rotation.

EXPERIMENTAL

A sample of pentafluorobenzaldehyde was obtained from Bristol Organics Ltd., and used without further purification. The liquid crystal used was Merck Phase IV. Attempts to obtain an n.m.r. spectrum of the molecule in the nematogen *N*-*p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA), and other similar Schiff's bases, led to a reaction between solute and solvent. The proton and fluorine spectra were recorded on a JEOL PS 100 spectrometer, using an external lock, and the continuous wave mode of operation. Line positions were measured to an accuracy of *ca.* 1 Hz. The Figure shows the observed and calculated fluorine spectrum.

An i.r. spectrum was recorded on a Perkin-Elmer 225, and Raman spectra on a Cary 81 spectrometer.

RESULTS AND DISCUSSION

Spectral Analysis.—The Hamiltonian used to analyse the spectra is, in frequency units, given by equation (1)

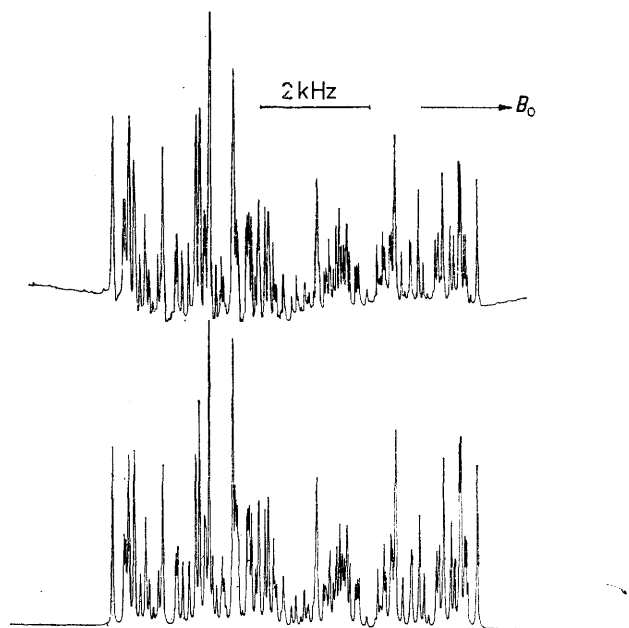
$$\mathcal{H} = - \sum_i \nu_i I_{zi} + \sum_{i < j} (J_{ij} + 2T_{ij}) I_{zi} I_{zj} + \frac{1}{2} \sum_{i < j} (J_{ij} - T_{ij}) (I_{+i} I_{-j} + I_{-i} I_{+j}) \quad (1)$$

where T_{ij} is the total anisotropic coupling constant, and may have contributions from dipolar coupling, D_{ij} , and

the anisotropic part J_{ij}^{aniso} of the spin-spin coupling tensor J_{ij} . Thus equation (2) is obtained.

$$T_{ij} = D_{ij} + \frac{1}{2} J_{ij}^{\text{aniso}} \quad (2)$$

The analyses were carried out with the aid of the computer program LAOCN 3, modified to include



Observed (upper) and calculated fluorine n.m.r. spectra of pentafluorobenzaldehyde dissolved in the nematogen Merck Phase IV

anisotropic coupling. The fluorine spectrum contains all the couplings and was used to provide a single set of coupling constants. The isotropic couplings, J_{ij} , were taken from the work of Dean and McFarlane,² and were

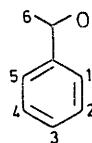
¹ P. Diehl, P. M. Henrichs, and W. Niederberger, *Org. Magnetic Resonance*, 1971, **3**, 243.

² R. R. Dean and W. McFarlane, *J. Chem. Soc. (B)*, 1969, 509.

kept constant. A total of 132 lines were assigned in the fluorine spectrum and used in the iterative part of the program, leading to a final r.m.s. error of 2.1 Hz, and the values shown in Table 1.

TABLE 1

N.m.r. parameters obtained from the analysis of the ^{19}F spectrum of a sample of pentafluorobenzaldehyde dissolved in the nematogen Merck Phase IV



Chemical shifts (p.p.m.)

$$\delta_2 - \delta_1 = 22.52$$

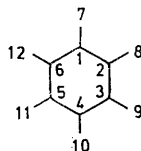
$$\delta_2 - \delta_3 = 20.94$$

Coupling constants (Hz)

	Anisotropic	Isotropic (from ref. 2)
1,2	-1 047.2 ± 0.4	-20.5
1,3	-162.3 ± 0.2	6.5
1,4	-73.9 ± 0.3	9.7
1,5	-74.1 ± 0.3	-4.9
1,6	-730.1 ± 0.2	1.0
2,3	-553.2 ± 0.2	-19.5
2,4	-74.6 ± 0.6	-1.2
2,6	-127.9 ± 0.2	-1.3
3,6	-88.3 ± 0.3	0.2

TABLE 2

Force field for hexafluorobenzene



Internal co-ordinate	Force constant *	Example
R_{CC}	5.749 mdyne \AA^{-1}	
R_{CF}	6.949 mdyne \AA^{-1}	
α_{CCC}	1.334 mdyne $\text{\AA} \text{ rad}^{-2}$	
α_{CCF}	0.632 mdyne $\text{\AA} \text{ rad}^{-2}$	
γ_{CF}	0.500 mdyne $\text{\AA} \text{ rad}^{-2}$ (out-of-plane wag)	
τ_{CCCC}	0.001 mdyne $\text{\AA} \text{ rad}^{-2}$ (CCCC torsion)	
τ_{CCCF}	0.103 mdyne $\text{\AA} \text{ rad}^{-2}$ (FCCF torsion)	
Interaction constants		
$R_{CC} R_{CC}$	(ortho) 1.216 mdyne \AA^{-1}	$R_{28} \alpha_{123}$
	(meta) 0.159 mdyne \AA^{-1}	$R_{12} \alpha_{712}$
	(para) 1.212 mdyne \AA^{-1}	$R_{12} \alpha_{123}$
$R_{CF} R_{CF}$	(ortho) -0.286 mdyne \AA^{-1}	$\alpha_{712} \alpha_{128}$
	(meta) -0.484 mdyne \AA^{-1}	$\alpha_{712} \alpha_{932}$
	(para) -0.393 mdyne \AA^{-1}	$\alpha_{712} \alpha_{9410}$
$R_{CF} \alpha_{CCC}$	-1.052 mdyne rad^{-1}	$\alpha_{128} \alpha_{823}$
$R_{CC} \alpha_{CCF}$	-0.250 mdyne rad^{-1}	$\alpha_{123} \alpha_{934}$
$R_{CC} \alpha_{CCF}$	0.024 mdyne rad^{-1}	
$\alpha_{CCF} \alpha_{CCF}$	0.020 mdyne $\text{\AA} \text{ rad}^{-2}$	
	0.050 mdyne $\text{\AA} \text{ rad}^{-2}$	
	-0.003 mdyne $\text{\AA} \text{ rad}^{-2}$	
	-0.315 mdyne $\text{\AA} \text{ rad}^{-2}$	
$\alpha_{CCC} \alpha_{CCF}$	0.286 mdyne $\text{\AA} \text{ rad}^{-2}$	
$\gamma_{CF} \gamma_{CF}$	(ortho) -0.148 mdyne $\text{\AA} \text{ rad}^{-2}$	
	(meta) 0.048 mdyne $\text{\AA} \text{ rad}^{-2}$	
	(para) 0.055 mdyne $\text{\AA} \text{ rad}^{-2}$	
$\tau_{CCCC} \tau_{CCCC}$	0.074 mdyne $\text{\AA} \text{ rad}^{-2}$	$\tau_{1234} \tau_{2345}$
$\tau_{CCCC} \tau_{CCCF}$	0.288 mdyne $\text{\AA} \text{ rad}^{-2}$	$\tau_{1234} \tau_{8239}$
$\gamma_{CF} \tau_{CCCF}$	0.045 mdyne $\text{\AA} \text{ rad}^{-2}$	$\gamma_{17} \tau_{6123}$

* mdyne $\text{\AA}^{-1} \equiv \text{N m}^{-1}$, mdyne $\equiv \text{N} \times 10^{-10}$, mdyne $\text{\AA} \equiv \text{N m} \times 10^{-20}$.

Vibrational Analysis.—Dipolar couplings are averaged over vibrational modes, and in order to include such effects in our analysis of the relationship between dipolar couplings and structure it is necessary to calculate the matrix $L_{ik\alpha}$ connecting normal co-ordinates Q_k of the k vibrational modes to cartesian displacement co-ordinates α_i of the i th atom.³ Our approach has been essentially theoretical in that the $L_{ik\alpha}$ values have been calculated using a valence force field based on force constants found to give a good fit to the frequencies of vibration of benzaldehyde⁴ and hexafluorobenzene. However, i.r. and Raman spectra were recorded of pentafluorobenzaldehyde and a tentative partial assignment made between observed and calculated frequencies, as shown in Table 5. In Table 2 are the force constants

TABLE 3

Observed (ref. 5) and calculated vibrational frequencies of hexafluorobenzene

Symmetry	Observed (cm^{-1})	Calculated (cm^{-1})
A_{1g}	1 490	1 503
	559	522
A_{2g}	691	691
B_{2g}	714	742
	249	231
E_{1g}	370	370
E_{2g}	1 655	1 656
	1 158	1 159
	443	458
	264	228
A_{2u}	215	215
B_{1u}	1 323	1 323
	640	640
B_{2u}	1 253	1 254
	208	202
E_{1u}	1 530	1 534
	1 019—994	1 001
	315	313
E_{2u}	595	590
	175	164

derived for hexafluorobenzene, and Table 3 compares observed and calculated frequencies. The force constants are based on those proposed by Steele and Whiffen⁵ and refined to give a closer fit to the observed frequencies using the computational method of Beattie *et al.*⁶ The force field used for pentafluorobenzaldehyde shown in Table 4 simply combines those derived from hexafluorobenzene and benzaldehyde.

Structure derived from Dipolar Couplings.—We assume that all J_{ij}^{aniso} are zero, hence T_{ij} can be equated to dipolar couplings, which are related to structure *via* relationship (3) where $\theta_{ij\alpha}$ is the angle between r_{ij} and

$$D_{ij} = \frac{-\gamma_i \gamma_j \hbar}{8\pi^2 r_{ij}^3} [S_{zz}(3\cos^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy})] - \frac{\gamma_i \gamma_j \hbar}{8\pi^2} [S_{zz}(2f_{ijzx} - f_{ijxx} - f_{ijyy}) + (S_{xx} - S_{yy})(f_{ijxx} - f_{ijyy})] \quad (3)$$

³ N. J. D. Lucas, *Mol. Phys.*, 1971, **22**, 233.

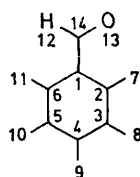
⁴ R. Zwarich, J. Smolarek, and L. Goodman, *J. Mol. Spectroscopy*, 1971, **38**, 336.

⁵ D. Steele and D. H. Whiffen, *Trans. Faraday Soc.*, 1959, **55**, 369.

⁶ I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc. (A)*, 1971, 2240.

the α th molecule-fixed axis. The terms $f_{ij\alpha\alpha}$ allow for averaging over vibrational modes, as discussed by Lucas.³ The ordering matrix $S_{\alpha\beta}$ is as defined by Saupe.⁷

TABLE 4
Force field for pentafluorobenzaldehyde



Internal co-ordinate	Force constant *	Example
R_{CC} (ring)	5.749 mdyne \AA^{-1}	
R_{CF}	6.949 mdyne \AA^{-1}	
α_{CCF}	0.632 mdyne $\text{\AA} \text{ rad}^{-2}$	
α_{CCC}	1.334 mdyne $\text{\AA} \text{ rad}^{-2}$	
γ_{CF}	0.500 mdyne $\text{\AA} \text{ rad}^{-2}$	
τ_{CCCC}	0.001 mdyne $\text{\AA} \text{ rad}^{-2}$	
τ_{FCCF}	0.103 mdyne $\text{\AA} \text{ rad}^{-2}$	
R_{CO}	10.772 mdyne \AA^{-1}	
R_{CH}	4.253 mdyne \AA^{-1}	
R_{CC} (i.e. $R_{1,14}$)	4.500 mdyne \AA^{-1}	
α_{CCO}	1.000 mdyne $\text{\AA} \text{ rad}^{-2}$	
α_{CCH}	0.400 mdyne $\text{\AA} \text{ rad}^{-2}$	
α_{HCO}	0.147 mdyne $\text{\AA} \text{ rad}^{-2}$	
γ_{CH}	0.251 mdyne $\text{\AA} \text{ rad}^{-2}$	
γ_{CO}	0.065 mdyne $\text{\AA} \text{ rad}^{-2}$	
τ_{HCCC}	0.005 mdyne $\text{\AA} \text{ rad}^{-2}$	
$R_{CC} R_{CC}$	<i>ortho</i> 1.216 mdyne \AA^{-1}	
	<i>meta</i> 0.159 mdyne \AA^{-1}	
	<i>para</i> 1.212 mdyne \AA^{-1}	
$R_{CF} R_{CF}$	<i>ortho</i> -0.286 mdyne \AA^{-1}	
	<i>meta</i> -0.484 mdyne \AA^{-1}	
	<i>para</i> -0.393 mdyne \AA^{-1}	
$R_{CC} R_{CO}$	0.750 mdyne \AA^{-1}	$R_{6,14} R_{14,13}$
$R_{CF} \alpha_{CCC}$	-1.052 mdyne rad^{-1}	$R_{28} \alpha_{123}$
$R_{CC} \alpha_{CCF}$	-0.250 mdyne rad^{-1}	$R_{12} \alpha_{712}$
$R_{CC} \alpha_{CCC}$	0.024 mdyne rad^{-1}	$R_{12} \alpha_{123}$
$\alpha_{CCF} \alpha_{CCF}$	0.020 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{712} \alpha_{128}$
	0.050 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{712} \alpha_{932}$
	-0.003 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{712} \alpha_{34,10}$
	-0.315 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{128} \alpha_{823}$
	-0.045 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{612} \alpha_{123}$
$\alpha_{CCC} \alpha_{CCF}$	0.286 mdyne $\text{\AA} \text{ rad}^{-2}$	$\alpha_{123} \alpha_{934}$
$\gamma_{CF} \gamma_{CF}$	<i>ortho</i> -0.148 mdyne $\text{\AA} \text{ rad}^{-2}$	$\gamma_{17} \gamma_{28}$
	<i>meta</i> 0.048 mdyne $\text{\AA} \text{ rad}^{-2}$	$\gamma_{17} \gamma_{39}$
	<i>para</i> 0.055 mdyne $\text{\AA} \text{ rad}^{-2}$	$\gamma_{17} \gamma_{4,10}$
$\tau_{CCCC} \tau_{CCCC}$	0.074 mdyne $\text{\AA} \text{ rad}^{-2}$	$\tau_{1234} \tau_{2345}$
$\tau_{CCCC} \tau_{FCCF}$	0.288 mdyne $\text{\AA} \text{ rad}^{-2}$	$\tau_{1234} \tau_{8239}$
$\gamma_{CF} \tau_{CCCC}$	0.045 mdyne $\text{\AA} \text{ rad}^{-2}$	$\gamma_{17} \tau_{6123}$

The internal motion of the formyl group about the C-C bond has been assumed to have a frequency, ν_{int} , which is much faster than the overall reorientational frequency of the molecule in the liquid crystal. Also, the molecule is assumed to be a rigid rotor, resulting in an effective mirror plane perpendicular to the ring plane and passing through C-1 and -4. With these assumptions there are six unknown co-ordinates specifying the relative positions of the five fluorines and the formyl proton, two independent $S_{\alpha\alpha}$ elements, and at least one parameter is needed to specify the nature of the internal rotation. One internuclear distance has to be assumed, and we have chosen this to be $r_{12} = 2.73 \text{ \AA}$, a value appropriate to hexafluorobenzene having $r_{C-C} = 1.40$ and $r_{C-F} = 1.33 \text{ \AA}$. There are nine observed couplings, hence it should be possible to determine the relative positions of

the interacting nuclei, and to test various models of internal rotation.

Consider first free rotation of the formyl group. A set of co-ordinates consistent with this model can be obtained, which give values of the residuals $\Delta D_{ij} = D_{ij}(\text{obs}) - D_{ij}(\text{calc.})$ which are similar to the best obtained for other models. However, the formyl proton is placed such that the C-H bond length in CHO is $>2.5 \text{ \AA}$, and hence the model is unrealistic. We conclude that there must be appreciable barriers to

TABLE 5
Observed and calculated vibrational frequencies of pentafluorobenzaldehyde
Observed (cm^{-1})

Symmetry	I.r.	Raman	Calculated
a'	2 885		2 807
	1 710	1 715	1 772
	1 650	1 657	1 676
	1 630	1 640	1 620
	1 520	1 526	1 541
	1 495	1 505	1 519
	1 400	1 405	1 447
	1 315	1 320	1 309
	1 270	1 273	1 261
	1 150	1 160	1 143
	1 130	1 136	1 094
	1 000	1 000	1 034
	945	947	1 011
	807		799
		775	756
	632	633	650
		597	567
	496	495	507
	443	440	453
	386		381
	323	320	307
			271
			233
			215
			176
a''			967
			730
			579
			558
	386	385	371
	360	358	354
	278	280	232
		215	208
		190	168
			164
			72
	58 *		

* S. Fewster, Ph.D. Thesis, Manchester University, 1970.

rotation about the C-C bond. The potential energy, $V(\theta)$, can be written as (4) where θ is the angle of rotation

$$V(\theta) = \frac{V_2}{2}(1 - \cos 2\theta) + \frac{V_4}{2}(1 - \cos 4\theta) + \dots \quad (4)$$

about the C-C bond, such that for $\theta = 0$ and 180° the formyl group lies in the plane of the aromatic ring. Assuming that the terms V_4 and higher are all zero, then two simplified models for the formyl rotation exist. A negative value of V_2 implies a minimum in $V(\theta)$ at $\theta = \pi/2$, and when V_2 has a large enough magnitude the molecule will exist predominantly in the two forms having the formyl group perpendicular to the ring. An

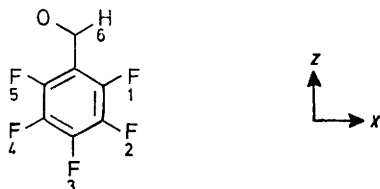
⁷ A. Saupe, *Z. Naturforsch.*, 1964, **19a**, 161.

attempt to derive a geometry for this model led to very large residuals (>50 Hz) and an unrealistic structure. The data, therefore, are not consistent with this model.

If V_2 is large and positive the molecule exists as an average of the two planar forms, and a test of this model gave the results shown in Table 6. The geometry

TABLE 6

Structural and orientation parameters for pentafluorobenzaldehyde assuming it to exist only in planar forms. The distance r_{12} has been fixed at 2.73 Å



	With vibrational averaging	Without	Standard * geometry
x_1 †	2.299 ± 0.046	2.296 ± 0.045	2.364
x_1	4.217 ± 0.058	4.219 ± 0.057	4.095
x_2	2.306 ± 0.031	2.304 ± 0.030	2.364
x_2	1.487 ± 0.033	1.489 ± 0.033	1.365
x_3	0.0	0.0	0.0
x_3	0.0	0.0	0.0
x_6	1.113 ± 0.052	1.053 ± 0.052	0.979
x_6	6.299 ± 0.042	6.341 ± 0.041	6.066
S_{zz}	0.2012 ± 0.0003	0.2005 ± 0.0003	
$S_{xx} - S_{yy}$	0.3400 ± 0.0043	0.3400 ± 0.0043	
ΔD_{12}	0.2	0.2	
ΔD_{13}	-2.0	-2.0	
ΔD_{14}	4.8	4.9	
ΔD_{15}	-2.6	-2.7	
ΔD_{16}	0.1	0.1	
ΔD_{23}	-0.1	-0.1	
ΔD_{24}	0.1	0.2	
ΔD_{26}	-3.7	-3.7	
ΔD_{36}	9.3	9.2	
R.m.s. error (Hz)	4.7	4.7	

* Standard geometry has a regular hexagon ring with $r_{CC} = 1.4$, $r_{CF} = 1.33$, $r_{C-C}(\text{ring-aldehyde}) = 1.48$, $r_{C-H} = 1.08$ Å, and $\text{CCH} = 115^\circ$. † Å $\equiv 10^{-10}$ m.

obtained from the dipolar couplings is close to a structure derived using r_{C-H} bond lengths and angles found in similar molecules, but the discrepancies between the two structures are just too large to be acceptable. In particular the co-ordinates of the formyl proton imply

⁸ T. Iijima and S. Tsuchiya, *J. Mol. Spectroscopy*, 1972, **44**, 88.

⁹ J. Gerritsen, G. Koopmans, H. S. Rollema, and C. MacLean, *J. Magnetic Resonance*, 1972, **8**, 20.

a C-H bond length considerably in excess of 1.14 Å, the value found for acetaldehyde.⁸ Furthermore, some of the residuals are too large and clearly indicate that the model is unsatisfactory. Vibrational averaging has a negligible effect on the fluorine co-ordinates, but makes an appreciable difference to those of the proton.

Some refinements of the planar model have been explored to see if they give more acceptable results. First, finite values of V_2 were chosen in the range 4–30 kJ mol⁻¹, the two-fold rotational eigenvalue equation (Mathieu's equation) was solved and the rotational probabilities calculated for the formyl group. These were used to calculate weighted averages of the couplings D_{16} and D_{26} . The results are similar to those shown in Table 6, and in particular inclusion of non-planar forms increases the length predicted for the C-H bond, and the residuals increase. Thus a high value for V_2 still gives the most acceptable result. Secondly, the assumption of a rigid rotor was partially relaxed. A model was tested which allows the co-ordinates of F_1 and F_5 to differ which means that the equilibrium structures no longer have (yz) as a mirror plane. The internal rotation was still assumed to be faster than whole molecule reorientation, so that only two $S_{\alpha\alpha}$ values are necessary to describe the averages couplings. There are now an equal number of unknowns as dipolar couplings, hence all residuals become zero. The predicted geometry was found to be unsatisfactory, and this kind of non-rigid rotor cannot be the only explanation of the large residuals in Table 6.

The most probable explanation of the large residuals is that J_{FF}^{aniso} values are important. In other fluorobenzenes the magnitudes of J_{FF}^{aniso} have been found to be in the range ± 13 Hz,⁹ but values as high as 36 Hz have been found in fluoro-olefins.^{10,11} We conclude that the n.m.r. data supports a planar equilibrium structure for pentafluorobenzaldehyde, but that precise nuclear co-ordinates are not obtainable because of appreciable contributions of J_{FF}^{aniso} to the T_{FF} values.

We thank JEOL (U.K.) Ltd. for the loan of a PS 100 spectrometer. We also thank the S.R.C. for granting access to the computing facilities of the Atlas Laboratory.

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¹⁰ G. J. den Otter and C. MacLean, *Chem. Phys.*, 1974, **3**, 119.

¹¹ J. Bulthuis and C. MacLean, *Chem. Phys. Letters*, 1973, **21**, 611.