

Molecular Physics



ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: http://www.tandfonline.com/loi/tmph20

The hyperfine coupling constants of some fluorinated free radicals

A. Hudson & J.W.E. Lewis

To cite this article: A. Hudson & J.W.E. Lewis (1970) The hyperfine coupling constants of some fluorinated free radicals, Molecular Physics, 19:2, 241-251, DOI: 10.1080/00268977000101221

To link to this article: http://dx.doi.org/10.1080/00268977000101221

Ē		
Е		Н

Published online: 23 Aug 2006.



Submit your article to this journal 🖙





View related articles 🗹



Citing articles: 16 View citing articles 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=tmph20

The hyperfine coupling constants of some fluorinated free radicals

by A. HUDSON and J. W. E. LEWIS†

School of Molecular Sciences, The University of Sussex, Brighton, BN1 9QJ

(Received 28 November 1969)

The electron resonance spectra of some fluorobenzyl radicals and fluorobenzaldehyde radical anions are reported. The observed hyperfine coupling constants are discussed in terms of π -electron spin densities estimated from semi-empirical molecular orbital calculations. Only one isomer is observed in the spectrum of the *o*-fluorobenzaldehyde radical anion, whereas two isomers are observed in the meta compound.

1. INTRODUCTION

Many recent publications have been concerned with the measurement and interpretation of ¹⁹F hyperfine coupling constants in aromatic radicals and a substantial amount of experimental information has become available. However, much of the data in the literature involves molecules like the fluoronitrobenzene radical anions [1-3] which contain other heteroatoms apart from fluorine. The spectra of these radicals are often solvent dependent and are not ideally suited to theoretical investigation. Comparison of data from anions and cations suggests that charge effects are also important in fluorine containing radicals and there is a need for experimental results on some simpler systems.

The benzyl radical has been the subject of several E.S.R. investigations [4–6] and recently some of its heterocyclic analogues have been observed [7]. We have now used the same techniques [8] to obtain the spectra of some fluorobenzyl radicals. These neutral aromatic systems contain no heteroatom apart from fluorine and are thus more suitable for theoretical investigation than many of the radicals reported in previous work. The fluorinated triphenylmethyl radicals studied by a number of authors [9–12] are most analogous to the new species reported here. We have also recorded the spectra of some fluorobenzaldehyde radical anions. These are less suitable for theoretical investigation but show interesting conformational properties.

2. Experimental

The benzyl radicals were prepared by photolysis of solutions containing di-t-butyl peroxide and the corresponding fluorotoluene at -70° c using methods described previously [8]. The pentafluorobenzyl radical could be obtained from the reaction of methylpentafluorobenzene and t-butoxyl radicals but as discussed elsewhere [13] better spectra were obtained from pentafluorobenzylbromide and

[†] Present address: Kamerlingh Onnes Laboratorium, Nieuwsteeg 18, Leiden, The Netherlands.

triethylsilyl radicals:

AD 40

The benzaldehyde radicals were also generated photochemically by irradiation at room temperature of solutions of the parent aldehyde in methanol containing sodium methoxide [14, 15]. This method can also be used to form the radical anions of substituted nitrobenzenes [1] and we have employed it to record the spectra of the 2,4-difluoronitrobenzene and 2,5-difluoronitrobenzene radical anions in methanol. These have recently been reported in aprotic solvents by Fischer and Zimmerman [3]. The spectra of the monofluoronitrobenzene radical anions in methanol solutions have been published previously [1, 16].

Some of the spectra are shown in figures 1-3 together with computer simulated spectra obtained using the coupling constants in table 1. The assignments have been made by analogy with the unfluorinated species and on the basis of semiempirical molecular orbital calculations.



Figure 1. The low field half of the E.S.R. spectrum of the p-fluorobenzyl radical. The arrow marks the centre of the spectrum.



						The second se
Radical	<i>a</i> ₂	<i>a</i> 3	<i>a</i> 4	a5	<i>a</i> ₆	<i>a</i> ₇
C ₆ H ₅ CH ₂	5.14	1.75	6.14	1.75	5.14	16.35+
2-FC ₆ H ₄ CH ₂	8.17	1.80	6.48	1.80	5.36	16.58, 16.33+
3-FC ₆ H ₄ CH ₂	5.31	4 ·87	6.36	1.85	5.06	16.54
$4-FC_6H_4CH_2$	5.47	1.74	14.53	1.74	5.47	16.89+
C ₆ F ₅ CH ₂	9.5	4.9	17.1	4.9	9.5	16.80†
C ₆ H ₅ CHO ⁻	4.26	1.36	6.24	1.62	5.14	13.001
2-FC ₆ H ₄ CHO	6.46	1.27	5.34	1.67	4.97	13·94 <u>†</u>
4-FC ₆ H ₄ CHO ⁻	4.45	1.55	13.16	1.71	5.53	13·35±
C ₆ H ₅ NO ₂ -	3.52	1.14	3.71	1.14	3.52	13.60§
$2,4-F_2C_6H_3NO_2^-$	6.52	1.12	7.84	1.12	3.48	14·20§
2,5-F ₂ C ₆ H ₃ NO ₂ -	6.82	1.06	3.85	2.80	3.48	12.73§
-						-

 \uparrow CH₂ protons. \ddagger Aldehyde proton. \S^{14} N splitting. || Coupling constants from [15]. The carbonyl oxygen is adjacent to ring position 2.

Table 1. The hyperfine coupling constants in gauss of some fluorinated radicals and their hydrocarbon analogues.

3. Molecular orbital calculations

As a guide to the assignment of coupling constants, and also with the hope of providing an interpretation of the ¹⁹F coupling constants, we have performed semiempirical molecular orbital calculations of the π -electron spin distribution for most of the radicals studied. The methods used were firstly the approximate SCF theory of McLachlan [17] and secondly, for the benzyl radicals, unrestricted Hartree–Fock (UHF) calculations of the type suggested by Pople and Nesbet [18]. In the latter case spin annihilation of contaminating quartet states in the SCF wavefunctions was carried out as suggested by Amos and Snyder [19].

The parameters used in the McLachlan calculations were:

(a) Fluorine. $\alpha_{\rm F} = \alpha + 1.6\beta$, $\beta_{\rm CF} = 0.7\beta$, together with an auxiliary inductive parameter of 0.1β for the adjacent carbon atom [1].

(b) Carbonyl oxygen. $\alpha_0 = \alpha + 2 \cdot 8\beta$, $\beta_{CO} = 1 \cdot 6\beta$, A.I.P. on carbonyl carbon of $0 \cdot 1\beta$. The value of α for the ortho ring carbon adjacent to the carbonyl oxygen was reduced by $0 \cdot 1\beta$ to allow for the asymmetry introduced by restricted rotation of the aldehyde group [15].

(c) Nitro group [1]. $\alpha_N = \alpha + 2 \cdot 2\beta$, $\beta_{CN} = 1 \cdot 2\beta$, $\alpha_O = \alpha + 1 \cdot 88\beta$, $\beta_{NO} = 1 \cdot 67\beta$. The parameter λ in the McLachlan calculations was initially taken as 1.00 for the benzyl radicals and 1.2 for the other species. The calculations on the benzyl radicals gave poor results and to obtain a more realistic spin distribution were repeated using a modification suggested recently by Kulkarni and Trapp [20]. It is a common feature of calculations on the benzyl radical [4] that $\rho_p < \rho_o$ but experimentally the splitting from the para proton is significantly larger than that from the ortho positions. It was argued that the methylene carbon in benzyl is probably less electronegative than the ring carbons; by taking $\alpha_{CH_a} = \alpha - 0.75\beta$ and $\lambda = 1.2$ excellent agreement was obtained with the experimental spin distribution. It is difficult, however, to rationalize the use of a perturbation as large as -0.75β and it is with some misgivings that we have incorporated this modification in our calculations. The main justification is in the final results which are a considerable improvement on the previous treatment. In the UHF calculations the diagonal matrix elements U_{ii} for carbon were taken as -11.14 ev and β for a C-C bond was taken as -2.371 ev. The parameters for fluorine were taken from recent work by Ford [21]. One-centre electron repulsion integrals were calculated as suggested by Paolini [22] from $\gamma_{ii} = 3.294Z_i$, where Z_i is the Slater effective nuclear charge. For internuclear distances of less than 3.0 Å two-centre electron repulsion integrals were found from the charged spheres approximation; at longer distances they were estimated from the reciprocal of the internuclear separation [23].

The McLachlan spin densities gave good agreement with experimental proton hyperfine coupling constants when inserted into McConnell's relationship. This is not unexpected since the parameters used for the heteroatoms were those found by previous workers to give the best agreement between theory and experiment [1, 15, 20] in radicals closely related to those reported here. The UHF calculations on the benzyl radicals gave poorer results, presumably because no attempt was made to treat the methylene carbon differently from those in the ring.

Those features of the results necessary for a discussion of the ¹⁹F coupling constant are summarized in table 2. Only the spin densities on fluorine and the adjacent carbon atom are given since fluorination generally has little effect on the rest of the system [1, 2, 9], and values for the unfluorinated compounds are already in the literature [1, 15, 20].

Radical	$a_{ m F}$	$a_{ m F}/a_{ m H}$	$ ho c^{\dagger}$	ρ F †	$ ho_{\mathbf{F}}/ ho_{\mathbf{C}}$
$2-FC_6H_4CH_2$	8.17	1.59	0.1632	0.0062	0.0380
3-FC ₆ H ₄ CH ₂	(-)4·87	2.78	-0.0643	-0.0038 -0.0074	0.0239 0.1151 0.0240
4-FC ₆ H ₄ CH ₂	14.53	2.37	0.2122 0.1190†	0.0010 0.0010	0.0240 0.0547 0.0252
2-FC6H4CHO [−]	6 · 46	1.52	0.1633	0.0085	0.0521
4-FC ₆ H₄CHO [−]	13.16	2.11	0 • 1924	0.0118	0.0613
2-FC ₆ H ₄ NO ₂ -	6·53§	1.86	0.1356	0.0093	0.0686
$3-FC_6H_4NO_2^-$	(-)3.08§	2.70	-0.0508	-0.0057	0.1122
4-FC ₆ H ₄ NO ₂ −	8.04§	2.17	0.1449	0.0108	0.0745
$2,4-F_2C_6H_3NO_2^{-1}$	6.52	1.85	0.1357	0.0093	0.0685
,	7.84	2.11	0.1443	0.0108	0.0748
$2.5 - F_2C_6H_3NO_2^-$	6.83	1.94	0.1346	0.0092	0.0683
, <u> </u>	$(-)2 \cdot 80$	2.46	-0.0526	-0.0058	0.1103
			1		

[†] Calculated using McLachlan's method unless otherwise stated. The benzyl results are those obtained using the modification suggested by Trapp and Kulkarni [20].

‡ UHF calculation after spin annihilation.

§ From [1].

The values of $a_{\rm F}/a_{\rm H}$ for C₆F₅CH₂ are 1.85, 2.8 and 2.78 for the 2, 3 and 4 positions respectively.

Table 2. Theoretical spin densities and ¹⁹F hyperfine interactions.

4. Discussion

4.1. Radicals from fluorotoluenes

The spectrum of the p-fluorobenzyl radical (figure 1) was easily interpreted, but the less symmetrical ortho and meta compounds gave complicated spectra which could only be analysed with the aid of computer simulation. An interesting feature of the o-fluorobenzyl spectrum is that the two methylene protons are inequivalent. A similar but smaller effect probably occurs in the m-fluoro radical since the central lines of the nominally 1:2:1 triplet are broader than the outer ones but the difference is not resolved in our spectra. Similar effects have been found in heterocyclic analogues of the benzyl radical [7] and several other systems in which the methylene protons are not related by a plane of symmetry [24, and references therein].

The way in which this inequivalence arises can be understood in terms of the following qualitative discussion. In semi-empirical theories which involve σ - π separation unpaired spin can be introduced into the σ orbitals by means of configuration interaction. Alternatively it is possible to work within an unrestricted Hartree-Fock formalism: the introduction of one-centre exchange integrals, as in the INDO method [25], then gives rise directly to the unpaired spin in the σ orbitals which is reflected in the proton hyperfine coupling constants.

The familiar result of the configuration interaction treatment is that the proton coupling constant is related to the π -electron spin density by the McConnell relation $a_{\rm H} = Q_{\rm CH}{}^{\rm H}\rho_{\rm C}$ where [26]:

$$Q_{\rm CH}{}^{\rm H} \propto \sum_{k,l} \frac{\langle k\pi | \pi l \rangle}{E(k \to l)} \sigma_k(r_{\rm H}) \sigma_l^*(r_{\rm H}). \tag{1}$$

The proton coupling constant can thus be related to excitations from bonding orbitals, σ_k , to antibonding orbitals σ_l^* of energy $E(k \rightarrow l)$, and spin density is transferred to the σ system by the exchange integral $\langle k\pi | \pi l \rangle$. When applying this procedure to a methylene group in which the protons are related by a plane of symmetry, we can combine the σ orbitals of the two C-H bonds to form orbitals which are either symmetric or antisymmetric with respect to the plane. This places a restriction on the excitations allowed in (1) since σ_k and σ_l must both be of the same symmetry. It is clear that the product $\sigma_k(r_H)\sigma_l^*(r_H)$ then has the same value at each proton. Conversely, if σ_k and σ_l are of different symmetry, the product is positive at one proton and negative at the other. Removing the plane of symmetry, for example by introducing an ortho or meta substituent into the benzyl radical, leads to mixing of the symmetric and antisymmetric orbitals and introduces terms into (1) which differ in sign at the two protons. There is thus a different value of Q_{CH}^{H} for each proton.

A configuration interaction calculation has been performed on the allyl radical by Atherton and Hinchliffe [27] which does in fact give two distinct methylene proton coupling constants but the assignment is the reverse of that found experimentally [28]. It is possible by starting from a set of symmetric and antisymmetric σ orbitals and allowing them to mix under a perturbation to show that the terms which differ in sign at the two protons are very sensitive to the $\sigma \rightarrow \sigma^*$ excitation energies and hence to the basis of σ orbitals used in the calculation. The inequivalence can be calculated more straightforwardly by performing an INDO calculation [25], but insufficient work has been done for us to judge the reliability of such a treatment as a means of assignment.

4.2. Radicals from fluorobenzaldehydes

Well-resolved spectra were obtained from both the ortho and para fluoro compounds. As is usual in such radicals [15, 29, 30] restricted rotation of the aldehyde group causes an asymmetry in the π -electron spin distribution and all the

247

ring protons are inequivalent. The splittings from the aldehyde proton and the fluorine atom are very similar and the assignment given in table 1 could equally well be reversed.

The spectrum of the *o*-fluorobenzaldehyde radical anion shown in figure 3 can also be analysed in terms of a single species. We assign it to the *O*-trans isomer (I) which is expected to be less sterically hindered than the *O*-cis form (II).



A far infra-red study of the torsional bands of the parent aldehyde [31] indicates that the *O*-trans form is also favoured in the gas phase. The energy difference between the two forms should be greater in the radical because of repulsion between the negative charge on oxygen and the fluorine atom and also because of solvation of the oxygen atom by the hydroxylic solvent. The assignment of coupling constants in table 1 for the o-fluoro radical must be regarded as tentative in view of the similarity of a_F , a_2 and a_6 , and a_3 and a_5 .

We have also recorded spectra from solutions containing *m*-fluorobenzaldehyde. A complete analysis of the complicated patterns obtained has so far eluded us, but the spectra clearly arise from two isomers present in unequal amounts. Two isomers have been reported in the E.S.R. spectrum of the *m*-cyanoacetophenone radical anion [32]. An investigation of the infra-red spectra of *m*-chloro, *m*-bromo and *m*-iodobenzaldehyde has recently shown that in the neat liquids only small differences exist between the two isomers [33]. With the exception of the *m*-iodo compound, the *O*-cis forms are the more stable in accord with earlier work on the vapour phase [31]. It will be interesting to extend our work to include the other halogens and to make comparisons between the conformational properties of the radical anions and the neutral molecules.

4.3. Radicals from fluoronitrobenzenes

Strong spectra of the 2,4-difluoro and 2,5-difluoronitrobenzene radical anions were observed in methanol. The coupling constants are very similar to those found for the monofluoro radicals in the same solvent and we have included these in table 2 for comparison. The ratios of coupling constants are in good agreement with those recently reported in aprotic solvents [3].

4.4. Fluorine hyperfine interactions

The success of the McConnell relationship [26] in relating proton hyperfine coupling constants to π -electron spin densities, and the application of its extensions to ¹³C [34] and ¹⁴N [35] splittings, has produced many attempts to determine a similar relationship for ¹⁹F. Discussions of these attempts already exist [2, 9, 36] and we shall only summarize here the main conclusions.

Experimentally it is found that in many compounds fluorination does not markedly change the π -electron spin distribution which can therefore be estimated from the proton splittings in the unsubstituted radical [1, 2, 9, 12, 37]. This is the

case in the radicals studied here but not in the fluorinated [36] semiquinones recently studied by Geiger and Gulick or in partially fluorinated cations of aromatic hydrocarbons [38]. Single crystal studies [39], contact shifts in N.M.R. spectra [40, 41], linewidth variations [42] in E.S.R. spectra [2, 9, 26, 36], and careful measurements of higher than second-order shifts in hyperfine splittings [43] have all led to the conclusion that the signs of ¹⁹F splittings are positive in situations where those of protons are negative. A large number of the ¹⁹F splittings in the literature can be accounted for empirically by (2) with $Q^{F} = 50 \pm 10$ gauss:

$$a_{\rm F} = Q^{\rm F} \rho_{\rm C} \tag{2}$$

but this is largely fortuitous and such an equation has little theoretical justification. Single crystal measurements [39, 44–46] of ¹⁹F anisotropic hyperfine tensors demonstrate the presence of an appreciable spin density on the fluorine atom. It has also proved possible in a number of instances to estimate this ' local' spin density from the widths of E.S.R. [2, 36] or N.M.R. lines [41].

Consequently most attempts at interpreting fluorine coupling constants have used equation (3); for many compounds the ratio $\rho_{\rm F}/\rho_{\rm C}$ is approximately constant

$$a_{\rm F} = Q_{\rm CC}{}^{\rm F}\rho_{\rm CC} + Q_{\rm FF}{}^{\rm F}\rho_{\rm FF} \tag{3}$$

and then equation (2) successfully correlates the experimental data. Unfortunately no consistent set of $\sigma-\pi$ parameters have emerged and many values are in the literature [2, 9, 37, 39–41].

It has often been assumed that, by analogy with proton hyperfine interactions, the spin polarization term Q_{CC}^{F} should be negative, but as has been pointed out by Sinclair and Kivelson this contribution may well be positive because of the large 2s-2p promotion energy of fluorine [9]. This point is discussed in more detail in a recent paper by Jameson and Gutowsky [47]. A positive but small value has been obtained in an N.M.R. study in which both ρ_{C} and ρ_{F} were determined experimentally [41]. If Q_{CC}^{F} is indeed positive much smaller values of Q_{FF}^{F} are required to account for the observed positive coupling constants than formerly appeared necessary. Equation (3) is a simplified version of the more general result that $a_{F} = \text{tr} (Q\rho)$ and can be extended by the addition of terms involving the overlap spin density:

$$a_{\mathbf{F}} = Q_{\mathbf{C}\mathbf{C}}{}^{\mathbf{F}}\rho_{\mathbf{C}\mathbf{C}} + (Q_{\mathbf{C}\mathbf{F}}{}^{\mathbf{F}} + Q_{\mathbf{F}\mathbf{C}}{}^{\mathbf{F}})\rho_{\mathbf{C}\mathbf{F}} + Q_{\mathbf{F}\mathbf{F}}{}^{\mathbf{F}}\rho_{\mathbf{F}\mathbf{F}}.$$
(4)

Hinchliffe and Murrell [48] have calculated all the Q factors using an independent electron model for the σ electrons and conclude that the off-diagonal terms are important. A similar assertion had previously been made by Schastnev and Zhidomirov who wrote the overlap spin density as $(\rho_{C}\rho_{F})^{1/2}$ [49, 50].

Having summarized current theories of fluorine hyperfine interactions, we can now return to our own results. As we have already remarked fluorination has little effect on the spin distribution. In table 2 are listed values of $a_{\rm F}/a_{\rm H}$ for all of the radicals studied, $a_{\rm H}$ being taken from the unsubstituted compounds. The ratio is generally in the range 2–2.5 but significant variations occur and there is an apparent correlation between $a_{\rm F}/a_{\rm H}$ and the position of substitution with ortho < para < meta. It is of interest that the ratio of $a_{\rm F}/a_{\rm H}$ is also lowest for the ortho positions in fluorinated triphenylmethyl radicals but the order of the meta and para positions is the reverse of that found here [10, 12]. For tris(pentafluorophenyl)methyl the ratios are 1.09, 1.45 and 2.45, and in tris(2,6-difluorophenyl)methyl the ortho ratio is as low as 0.83.

These results indicate the limitations of a single parameter fit as represented by equation (2) and suggest that at least a two-term equation is required. The correlation of the values of $a_{\rm F}/a_{\rm H}$ with the position of substitution is encouraging since our radicals all have similar spin distributions. It implies that the values of $\rho_{\rm F}/\rho_{\rm C}$ are roughly constant for a given ring position but vary with the position of substitution. The results of the McLachlan spin density calculations support this point of view with low values of $\rho_{\rm F}/\rho_{\rm C}$ corresponding to low values of $a_{\rm F}/a_{\rm H}$. In contrast the UHF calculations give almost identical values of $\rho_{\rm F}/\rho_{\rm C}$ for the three monofluorobenzyl radicals. (The ratios are also lower than in the McLachlan calculations but this is of no significance because the absolute value of $\rho_{\rm F}$ is sensitive to the choice of parameters for the fluorine atom.) In a recent paper UHF calculations similar to those reported here have been performed [51] on a number of fluorine containing semiquinones [52] and nitrobenzene radical anions [1-3]. The ratios $\rho_{\rm FF}/\rho_{\rm CC}$ and $\rho_{\rm CF}/\rho_{\rm CC}$ were found to be approximately constant and the data could be fitted with $Q^{\mathbf{F}} = 54$ G when equation (4) was reduced to equation (2).

We regard the McLachlan spin densities as the more realistic although this may simply reflect a better choice of parameters for the heteroatoms. The N.M.R. results of Esperen and Kreilick [41] on a series of fluorine containing phenoxy radicals are of particular value in assessing theoretical calculations since both $\rho_{\rm C}$ and $\rho_{\rm F}$ were determined experimentally. For ortho, meta and para-fluoro phenyl substituents the ratios of $a_{\rm F}/a_{\rm H}$ were 1.64, 2.19 and 2.43 which correlate well with the experimental spin density ratios of 0.078, 0.106 and 0.119 respectively. As the next step in our analysis we might consider using the theoretical spin densities and the experimental coupling constants to determine the Q factors in equation (3) or (4). However, this procedure does not lead to a consistent set of σ - π parameters because the resulting equations are ill-conditioned and there are large uncertainties in the values of $\rho_{\rm F}$.

This conclusion is by no means original and it seems that until more accurate wavefunctions are available, experimental determinations of $\rho_{\rm C}$ and $\rho_{\rm F}$ offer the best hope of a solution. It is clear however that at least two terms are required to account for the ¹⁹F hyperfine couplings of the fluorobenzyl radicals, with the dominant positive contribution probably coming from $Q_{\rm FF}^{\rm F}$. $Q_{\rm CC}^{\rm F}$ may also be positive but there are a number of anomalously low coupling constants in the literature which are difficult to explain if both terms in equation (2) are positive. Eaton *et al.* have reported an *m*-fluoro radical in which $a_{\rm F}/a_{\rm H}$ is 0.17 [40]; the *m*-fluorine splittings in the radicals C₆F₅OCH₂ and *m*-FC₆H₄OCH₂ are less than the linewidths whereas resolvable splittings are obtained from the corresponding protonated radicals [53].

If there are no stereochemical factors involved which might give rise to unusual couplings, these low values are best accommodated in the theory if a cancellation of terms occurs. Configuration interaction estimates of $Q_{\rm CC}^{\rm F}$ show that its value is mainly determined by the difference between two large terms of opposite sign [48–50]. It may be that, because of changes in the nature of the C-F bond, $Q_{\rm CC}^{\rm F}$ is sometimes small and negative rather than small and positive. According to the calculations of Hinchliffe and Murrell [48] the overlap spin density makes a positive contribution to the coupling constant, in which case its inclusion will not explain a low hyperfine splitting. We conclude that although it is possible to give a reasonable qualitative discussion of ¹⁹F hyperfine interactions in aromatic radicals, more theoretical work needs to be done before a satisfactory quantitative treatment is

possible. The data reported in this paper should be a useful basis for these investigations.

We thank the S.R.C. for a Research Studentship to J. W. E. L. and a grant towards apparatus, Professor J. N. Murrell for helpful discussions and Dr. Alan Bowles for assistance with the molecular orbital calculations.

References

- [1] CARRINGTON, A., HUDSON, A., and LONGUET-HIGGINS, H. C., 1965, Molec. Phys., 9, 377.
- [2] KAPLAN, M., BOLTON, J. R., and FRAENKEL, G. K., 1965, J. chem. Phys., 42, 955.
- [3] FISCHER, P. H. H., and ZIMMERMANN, H., 1968, Can. J. Chem., 46, 3847.
- [4] CARRINGTON, A., and SMITH, I. C. P., 1965, Molec. Phys., 9, 137.
- [5] DIXON, W. T., and NORMAN, R. O. C., 1964, J. chem. Soc., p. 4857.
- [6] FISCHER, H., 1964, Z. Naturf. A, 20, 428.
- [7] HUDSON, A., HUSSAIN, H. A., and LEWIS, J. W. E., 1969, Molec. Phys., 16, 519.
- [8] HUDSON, A., and HUSSAIN, H. A., 1969, J. chem. Soc. B, p. 793.
- [9] SINCLAIR, J., and KIVELSON, D., 1968, J. Am. chem. Soc., 90, 5074.
- [10] TRAPP, C., WANG, C. S., and FILLER, R., 1966, J. chem. Phys., 45, 3472.
- [11] ALLENDOERFER, R. D., and MAKI, A. H., 1969, J. Am. chem. Soc., 91, 1088.
- [12] KULKARNI, S. V., and TRAPP, C., 1969, J. Am. chem. Soc., 91, 191.
- [13] HUDSON, A., and JACKSON, R. A., 1969, Chem. Commun., p. 1323.
- [14] AYSCOUGH, P. B., and WILSON, R., 1963, J. chem. Soc., p. 5412.
- [15] WILSON, R., 1966, Can. J. Chem., 44, 551.
- [16] CARRINGTON, A., HUDSON, A., and LUCKHURST, G. R., 1965, Proc. R. Soc. A, 284, 582.
- [17] McLachlan, A. D., 1960, Molec. Phys., 3, 233.
- [18] POPLE, J. A., and NESBET, R. K., 1954, J. chem. Phys., 22, 571.
- [19] AMOS, A. T., and SNYDER, L. C., 1965, J. chem. Phys., 42, 3670.
- [20] KULKARNI, S. V., and TRAPP, C., 1969, Molec. Phys., 17, 209.
- [21] FORD, B., 1968, Theor. chim. Acta, 10, 342.
- [22] PAOLINI, L., 1956, Nuovo Cim., 4, 410.
- [23] PARISER, R., and PARR, R. G., 1953, J. chem. Phys., 21, 466.
- [24] HUDSON, A., 1969, J. chem. Soc. A, p. 2513.
- [25] POPLE, J. A., BEVERIDGE, D. L., and DOBOSH, P. A., 1968, J. Am. chem. Soc., 90, 4201.
- [26] McConnell, H. M., 1958, J. chem. Phys., 28, 1188.
- [27] HINCHLIFFE, A., and ATHERTON, N. M., 1967, Molec. Phys., 13, 89.
- [28] KOCHI, J. K., and KRUSIC, P. J., 1968, J. Am. chem. Soc., 90, 7157.
- [29] MAKI, A. H., 1961, J. chem. Phys., 35, 761.
- [30] STEINBERGER, N., and FRAENKEL, G. K., 1964, J. chem. Phys., 40, 723.
- [31] MILLER, F. A., FATELY, W. G., and WITKOWSKI, R. E., 1967, Spectrochim. Acta A, 23, 891.
- [32] RIEGER, P. H., and FRAENKEL, G. K., 1962, J. chem. Phys., 37, 2811.
- [33] CROWDER, G. A., and NORTHAM, F., 1969, J. chem. Phys., 50, 4865.
- [34] KARPLUS, M., and FRAENKEL, G. K., 1961, J. chem. Phys., 35, 1312.
- [35] HENNING, J. C. M., 1966, J. chem. Phys., 44, 2139.
- [36] GEIGER, W. E., and GULICK, W. M., 1969, J. Am. chem. Soc., 91, 4657.
- [37] BROWN, J. K., and WILLIAMS, W. G., 1968, Trans. Faraday Soc., 64, 298.
- [38] FISCHER, P. H. H., and ZIMMERMANN, H., 1969, Tetrahedron Lett., p. 797.
- [39] COOK, R. J., ROWLANDS, J. R., and WHIFFEN, D. H., 1964, Molec. Phys., 7, 31.
- [40] EATON, D. R., JOSEY, A. D., PHILLIPS, W. D., and BENSON, R. E., 1962, *Molec. Phys.*, 5, 407. EATON, D. R., JOSEY, A. D., BENSON, R. E., PHILLIPS, W. D., and CAIRNS, T. L., 1962, *J. Am. chem. Soc.*, 84, 4100.
- [41] ESPEREN, W. G., and KREILICK, R. W., 1969, Molec. Phys., 16, 577.
- [42] HUDSON, A., and LUCKHURST, G. R., 1969, Chem. Rev., 69, 191.
- [43] FESSENDEN, R. W., and SCHULER, R. H., 1965, *J. chem. Phys.*, 43, 2704. FESSENDEN, R. W., 1969, *J. Mag. Res.*, 1, 277.
- [44] LONTZ, R. J., and GORDY, W., 1962, J. chem. Phys., 37, 1357.
- [45] ROGERS, M. T., and WHIFFEN, D. H., 1964, J. chem. Phys., 40, 2662.

251

- [46] LONTZ, R. J., 1966, J. chem. Phys., 45, 1339.
- [47] JAMESON, C. J., and GUTOWSKY, H. S., 1969, J. chem. Phys., 51, 2790.
- [48] HINCHLIFFE, A., and MURRELL, J. N., 1968, Molec. Phys., 14, 147.
- [49] SCHASTNEV, P. V., and ZHIDOMIROV, G. M., 1964, J. struct. Chem., 5, 778. [50] SCHASTNEV, P. V., and ZHIDOMIROV, G. M., 1967, J. struct. Chem., 8, 127.
- [51] RAY, N. K., 1969, Chem. Phys. Lett., 3, 261.
- [52] FISCHER, P. H. H., and ZIMMERMAN, H., 1968, Z. Naturf. A, 23, 1399.
- [53] HUDSON, A., and ROOT, K. D. J., 1970, J. chem. Soc. B, 656.