

Relationships for assigning Isotropic Hyperfine Coupling Constants for a Variety of Aromatic Radicals

By David Greatorex, H. Donald B. Jenkins* and Terence J. Kemp,* Department of Molecular Sciences, University of Warwick, Coventry CV4 7AL

Twenty-four aromatic radicals, supposedly capable of distortion from the classical regular hexagonal shape, are subjected to spin density calculations incorporating such a slight distortion with the results that (i) enhanced correlation of experimental and calculated hyperfine coupling constants is achieved and (ii) that elaboration of the McConnell equation is unnecessary.

BENSON *et al.*¹ have considered the effect on the calculated hyperfine coupling constants of distortion of the classical regular hexagonal geometry of fluorobenzyl radicals. They obtained an optimised set of bond lengths consistent with the best theoretical-experimental correlation of these constants. Similar improvement in theoretical values obtained for proton coupling has been noted² when the benzyl radical is allowed to distort from regularity. The aim of the work reported here is twofold: (i) to adopt a slightly distorted model to the optimised one obtained in ref. 2 and (ii) to examine the applicability of such a model to a greater variety of radical types (both neutral and anionic) to establish the role of distortion. Our criteria for assessing the usefulness of the incorporation of distortion is improved correlation between theoretical and experimental coupling constants not only for ¹H but also for ¹⁴N and ¹⁹F.

THEORY

The method of calculation of spin densities employed in this work has been described in detail by Beveridge and Hinze.³ The unrestricted Hartree-Fock (UHF) procedure coupled with the annihilation technique of Amos and Snyder⁴ was used, being effectively an open-shell calculation of Type 2 as classified by Zeiss and Whitehead.⁵ The unpaired spin density, ρ_x on an atom X was calculated from the diagonal elements of the spin density matrix [equation (1)]. The definitions (2) where p is the

$$\rho_{uv} = \mathbf{p}_{uv}^{(\alpha)} - \mathbf{p}_{uv}^{(\beta)} \quad (1)$$

$$\mathbf{p}_{uv}^{(\alpha)} = \sum_{i=1}^p C_{ui}^{(\alpha)} C_{vi}^{(\alpha)} \quad (2)$$

occupation number of the molecular orbital, and (3)

$$\mathbf{p}_{uv}^{(\beta)} = \sum_{i=1}^q C_{vi}^{(\beta)} C_{ui}^{(\beta)} \quad (3)$$

where q is the occupation number of the molecular orbital apply. $C_{ui}^{(\alpha)}$ and $C_{vi}^{(\alpha)}$ are the coefficients of the u th and v th atoms in the i th molecular spin orbital containing electrons with spin α and $C_{ui}^{(\beta)}$ and $C_{vi}^{(\beta)}$ are the corresponding coefficients in the i th molecular spin orbital containing electrons with β spin.

Since it is claimed⁶ that the restricted Hartree-Fock configuration interaction method gives comparable results

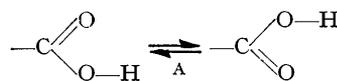
¹ H. G. Benson, A. Hudson, and J. W. E. Lewis, *Mol. Phys.*, 1971, **21**, 935.

² H. G. Benson and A. Hudson, *Mol. Phys.*, 1971, **20**, 185.

³ D. L. Beveridge and J. Hinze, *J. Amer. Chem. Soc.*, 1971, **93**, 3107.

to the UHF-annihilation procedure, we chose the latter since it is generally less time consuming.⁵

Parameterisation was identical to that suggested by Beveridge and Hinze³ except in so far that the two oxygen atoms in the carboxy-group (for the series of radical anions derived from aromatic carboxylic acids) were treated as equivalent, simple arithmetic means of the valence state ionisation potentials and of one-centre Coulomb integrals involving O ($tr^2tr^2tr\pi$) and O ($tr^2trtr\pi^2$) being taken in view of the known rapid dynamic isomerism Λ .



The regular hexagonal model employed as a reference consists of equalised bonds having a length of 0.140 nm whereas the distorted form referred to throughout this paper has bonds of length 0.142 and 0.138 nm respectively for 1-2, 1-6, 3-4, 4-5, and 2-3, 5-6 bonds (standard nomenclature).

In order to test the applicability of the optimised bond lengths developed for fluorobenzyl radical¹ to the present work as a basis for our 'distorted' model, we examined, for the case of the benzoic acid radical anion, the effects on ρ_4 , the calculated spin density at position 4 (the highest spin density and that most sensitive to the bond length variations considered) arising from simultaneous variation of the ring substituent C-C bond length, the 1-2 bond length (variations within the range 0.140-0.146 nm) and the 2-3 bond length (which was varied from 0.134 to 0.140 nm). Exact agreement with the experimental value for ρ_4 ⁷ is produced by the model having a ring substituent bond length 0.144, a 1-2 length of 0.142, and a 2-3 bond length of 0.138 nm and this particular configuration, which accords reasonably well with that used by Benson *et al.*¹ has been adopted for all the radicals dealt with here.

RESULTS

Proton Coupling Constants.—The McConnell relation⁸ when constrained to the origin takes the form (4) and

$$a_H = Q_C^H \rho_C \quad (4)$$

relates the proton coupling constant a_H to the π electron spin density ρ_C on the adjacent carbon atom. Values of Q_C^H , the σ - π interaction parameter, obtained by various

⁴ T. Amos and L. C. Snyder, *J. Chem. Phys.*, 1964, **41**, 1773.

⁵ G. D. Zeiss and M. A. Whitehead, *J.C.S. Faraday II*, 1972, **68**, 526.

⁶ J. Tino, *Theor. Chim. Acta*, 1970, **18**, 119.

⁷ A. R. Buick, T. J. Kemp, G. T. Neal and T. J. Stone, *J. Chem. Soc. (A)*, 1970, 227.

⁸ H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 1188.

workers have ranged from -1.0 to -2.5 mT,^{5,9} a typical value being -2.3 mT.¹⁰

The unconstrained McConnell relationship (5) where C

$$a_H = Q_C^H \rho_C + C \quad (5)$$

is a constant, the Colpa-Bolton relation (6)^{11a} where

$$a_H = Q_C^H \rho_C + K^H \epsilon \rho_C \quad (6)$$

Q_C^H is the value of the σ - π interaction parameter for a carbon atom with a zero excess charge and the excess charge ϵ is given by (7) where q_i is calculated from the

$$\epsilon = 1 - q_i \quad (7)$$

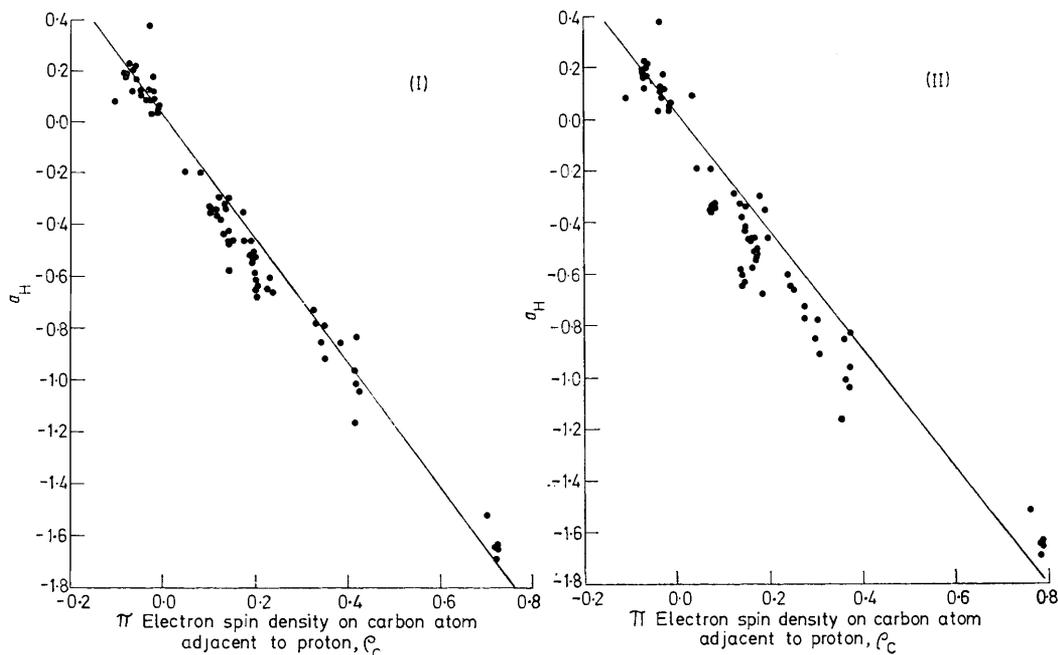
diagonal elements of the bond order matrix $q_{uv} = P_{uv}^{(\alpha)} + P_{uv}^{(\beta)}$ and the Giacometti-Nordio-Pavan relation (8)^{11b}

$$a_H = Q_C^{H''} \rho_C + Q_{CC}^{H''} \sum \rho_{CC_i} \quad (8)$$

(where the summation is carried out over next-nearest neighbours, and $Q_C^{H''}$ and $Q_{CC}^{H''}$ are empirical curve fitting parameters) have been considered as parametric equations

aromatic free radicals yielded values of Q_C^H in equation (4) of -2.39 (regular model) and -2.44 mT (distorted model) (Figure) with estimated standard deviations (e.s.d.'s) of 0.14 and 0.10 mT respectively. The unconstrained McConnell equation (5) yields Q_C^H values of -2.23 and -2.32 mT respectively for the two cases with e.s.d.'s of 0.124 and 0.094 mT.

The superiority of the other parameter schemes, namely, the Colpa-Bolton and Giacometti-Nordio-Pavan method over the simple McConnell method is not evident from our results. Fitting the results of the calculations reported here to the relationships (6) and (8) yielded, for the distorted geometry, $a_H = -2.367\rho_C - 1.827\epsilon\rho_C$ (e.s.d. 0.088 mT) for neutral radicals, and for anionic radicals yielded $a_H = -3.123\rho_C - 3.521\epsilon\rho_C$ (e.s.d. 0.070 mT), and for the two parameter expression (8) $a_H = -2.518\rho_C - 0.277 \sum_i \rho_{CC_i}$ (e.s.d. 0.099 mT) where the e.s.d.'s cited are errors in the calculated hyperfine coupling, a_H . The results of the calculations are given in Supplementary Publication SUP No 20753 (7 pp.).*



Correlation of experimental coupling constants a_H with π electron spin densities ρ_C calculated (I) for distorted model and (II) for regular hexagon

for interpretation of our results. C and K^H are constants fitted by least squares analysis, ϵ is the excess π -electron density on the carbon atom adjacent to the proton and $Q_C^{H''}$, $Q_{CC}^{H''}$, and ρ_{CC_i} are, respectively, the σ - π interaction terms usually treated as empirical curve fitting parameters and the interactive π electron spin density between the carbon atom adjacent to the proton and the next nearest neighbouring carbon atom C_i .

The calculations reported here on 24 neutral and anionic

* For details of Supplementary Publications see *J.C.S. Dalton*, 1972, Index Issue. Items less than 10 pp. are supplied as full size copies.

⁹ J. E. Bloor, B. R. Gilson, and D. D. Shillady, *J. Phys. Chem.*, 1967, **71**, 1238.

¹⁰ J. A. Pople, D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, p. 146.

Fluorine Coupling Constants.—To correlate measured fluorine coupling constants with spin densities, three relationships were examined: (i) the Anderson-Frank-Gutowski¹² relationship (9) (also proposed by Maki and Geske¹³) where a_F is the fluorine hyperfine coupling constant,

$$a_F = Q_C^F \rho_C \quad (9)$$

stant, Q_C^F is the σ - π interaction parameter for the carbon atom adjacent to the fluorine atom (normally of the order

¹¹ (a) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 1963, **6**, 273; (b) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theor. Chim. Acta*, 1963, **1**, 404.

¹² D. H. Anderson, P. J. Frank, and H. S. Gutowski, *J. Chem. Phys.*, 1960, **32**, 196.

¹³ A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

of 6.0 mT) and ρ_C is the spin density on the carbon atom; (ii) the Eaton-Josey-Phillips-Benson-Cairns relationship (10)^{14,15} (also examined by other workers^{16,17}) where

$$a_F = Q_{FF}^F \rho_F + Q_{CF}^F \rho_C \quad (10)$$

Q_{FF}^F , Q_{CF}^F are the σ - π interaction parameters for the fluorine and carbon atoms respectively and ρ_F and ρ_C are respective spin densities on the fluorine and carbon atoms; and (iii) the Schastnev and Zhidomirov relation (11)¹⁸ for

$$a_F = Q_{FF}^F \rho_F + Q_{CF}^F \rho_C + Q_{CF}^F \rho_{CF} \quad (11)$$

which widely varying values of Q_{FF}^F , Q_{CF}^F , and Q_{CF}^F (the σ - π interaction parameters for the fluorine and carbon atoms and the C-F bond respectively) exist.¹⁹ ρ_{CF} is the spin density in the C-F bond calculated as the off-diagonal term in the spin density matrix.

The optimum parameterisation according to the present

magnitude of ρ_F , suggesting that the parameterisation for the fluorine atom, as proposed by Beveridge and Hinze³ is not optimised. We have used the parameters of Ford²² assuming the valence state ionisation potential of Paolini²³ and obtained higher spin densities on fluorine without greatly affecting the spin densities in the carbon skeleton (see Table 1). Lowering the ionisation potential further results in an increase in π density on the fluorine atom. The results, taking an ionisation potential of 29.0 eV, show favourable agreement with INDO and experimental results but further work is required to optimise the value of 40.7 eV proposed by Beveridge and Hinze³ as this seems too high to reproduce meaningful spin densities at the fluorine atom.

Table 1 shows the theoretical and experimental coupling constants using the various schemes for the distorted model.

TABLE 1

Fluorine hyperfine couplings: comparison of experimental and calculated values using the distorted model (in mT)

Radical (or radical anion)	a_F (Experimental)	a_F (Calculated)			Equation with Ford-Paolini parameters
		Equation (9)	Equation (10)	Equation (11)	
3-FC ₆ H ₄ CO ₂ H	-0.322	-0.238	-0.228	-0.211	-0.051
4-FC ₆ H ₄ CO ₂ H	1.745	2.030	1.821	1.920	0.344
2-FC ₆ H ₄ CN	0.554	0.752	0.702	0.547	0.166
3-FC ₆ H ₄ CN	-0.251	-0.181	-0.176	-0.169	-0.040
3-FC ₆ H ₄ CN	2.296	2.166	2.013	2.054	0.410
2-FC ₆ H ₄ O	1.700	1.464	1.682	1.694	0.440
4-FC ₆ H ₄ O	2.740	2.762	2.762	2.757	0.651
2-FC ₆ H ₄ CH ₂	0.817	1.174	1.175	1.167	0.268
3-FC ₆ H ₄ CH ₂	-0.487	-0.568	-0.581	-0.580	-0.135
4-FC ₆ H ₄ CH ₂	1.453	1.221	1.284	1.332	0.302
2-FC ₆ H ₄ NO ₂	0.653	0.585	0.606	0.605	0.143
3-FC ₆ H ₄ NO ₂	-0.308	-0.351	-0.330	-0.311	-0.071
4-FC ₆ H ₄ NO ₂	0.841	0.686	0.664	0.658	0.145
2-FC ₅ H ₄ N	0.712	1.005	0.939	0.728	0.222

work would seem to be, for the one-parameter scheme (9) applied to the regular model, $a_F = 6.806 \rho_C$ (e.s.d. 0.326 mT), and for the distorted model, $a_F = 6.207 \rho_C$ (e.s.d. 0.203 mT). For the two-parameter scheme (10) (regular model) $a_F = 114.760 \rho_F + 5.355 \rho_C$ (e.s.d. 0.305 mT) and (distorted model) $a_F = 108.142 \rho_F + 4.930 \rho_C$ (e.s.d. 0.170 mT). The three parameter model gives (regular model) $a_F = 63.086 \rho_F + 4.870 \rho_C - 0.546 \rho_{CF}$ (e.s.d. 0.304 mT) and (distorted model) $a_F = 825.83 \rho_F + 7.833 \rho_C + 50.217 \rho_{CF}$ (e.s.d. 0.150 mT).

Theoretical estimation of Q_{FF}^F , Q_{CF}^F , and Q_{CF}^F by Schastnev and Zhidomirov¹⁸ yielded values of 26.4, 0.4 and -6.4 mT. Experimental measurement using n.m.r. line shapes^{20,21} yields values of $Q_{CF}^F = 0.62$ and $Q_{FF}^F = 49.7$ mT; however, for radicals where $\rho_F \propto \rho_C$, both sets of results reduce to the one-parameter equation (9) with a Q_{CF}^F value of ca. 6.0 mT, in agreement with our results. It is clear then that our discrepancy lies in the

Nitrogen Coupling Constants.—Three relationships were examined to correlate theoretical π -electron spin densities and measured hyperfine coupling constants: (i) the Carrington and dos Santos-Veiga²⁴ relation (12), which is similar to the McConnell relation for proton couplings, the definitions of the various parameters being analogous

$$a_N = Q_{FN}^N \rho_N \quad (12)$$

to the fluorine case; (ii) the Karplus-Fraenkel relation (13)²⁵ where ρ_{X_i} is the spin density on the neighbouring

$$a_N = Q_{FN}^N \rho_N + Q_{FX}^N \sum_i \rho_{X_i} \quad (13)$$

atom X_i ; and (iii) the Yonezawa, Kawamura, and Kato²⁶ method which takes into account spin density terms ρ_{NX} in the bonds between nitrogen and neighbouring atoms, X.

$$a_N = Q_{FN}^N \rho_N + Q_{FX}^N \sum_i \rho_{X_i} + Q_{NX}^N \sum_i \rho_{NX_i} \quad (14)$$

¹⁴ D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Amer. Chem. Soc.*, 1962, **84**, 4100.

¹⁵ D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 1962, **5**, 406.

¹⁶ A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, 1965, **9**, 377.

¹⁷ M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 955.

¹⁸ P. V. Schastnev and G. M. Zhidomirov, *Zhur. Strukt. Khim.*, 1964, **5**, 839.

¹⁹ P. H. H. Fischer and J. P. Colpa, *Z. Naturforsch.*, 1969, **24a**, 1980.

²⁰ W. G. Espersen and R. W. Kreilick, *Mol. Phys.*, 1969, **16**, 577.

²¹ S. Icli and R. W. Kreilick, *J. Phys. Chem.*, 1971, **75**, 3462.

²² B. Ford, *Theor. Chim. Acta*, 1968, **10**, 342.

²³ L. Paolini, *Il. Nuovo Cimento*, 1956, **4**, 410.

²⁴ A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, 1962, **5**, 21.

²⁵ M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

²⁶ T. Yonezawa, T. Kawamura and H. Kato, *J. Chem. Phys.*, 1969, **50**, 3482.

The results of our calculations are listed below.

(1) For the regular hexagonal model and a formal charge on the nitrogen atom of 2, equations (12)–(14) yield $a_N = 2.488 \rho_N$ (e.s.d. 0.129 mT), $a_N = 2.270 \rho_N + 0.327 \sum_i \rho_{X_i}$ (e.s.d. 0.089 mT), and $a_N = 1.471 \rho_N - 0.176 \sum_i \rho_{X_i} - 1.107 \sum_i \rho_{NX_i}$ (e.s.d. 0.013 mT), respectively; and for nitrogen atoms having a formal charge of 1, they yield $a_N = 1.668 \rho_N$ (e.s.d. 0.049 mT), $a_N = 1.859 \rho_N - 0.214 \sum_i \rho_{X_i}$ (e.s.d. 0.047 mT), and $a_N = 1.080 \rho_N - 1.109 \sum_i \rho_{X_i} - 1.292 \sum_i \rho_{NX_i}$ (e.s.d. 0.013 mT), respectively.

(2) For the distorted model with a formal charge of 2 on the nitrogen atom, they yield $a_N = 2.654 \rho_N$ (e.s.d. 0.124 mT), $a_N = 2.408 \rho_N + 0.370 \sum_i \rho_{X_i}$ (e.s.d. 0.076 mT), and $a_N = 1.918 \rho_N + 0.073 \sum_i \rho_{X_i} - 0.675 \sum_i \rho_{NX_i}$ (e.s.d. 0.067 mT), respectively; and for nitrogen atoms having a formal

charge of 1, the e.s.d. of the correlation. Contrary to our experience with nitrogen coupling constants, a general application of the Colpa–Bolton relationship (*i.e.* irrespective of anionic or neutral character of the radicals) is unsatisfactory for proton coupling constants and improvement occurs only when anionic and neutral radicals are considered separately.

Results on fluorine coupling constants showed that the Schastnev and Zhidomirov relation (11) offered improved correlation over that given by equations (9) and (10). Recourse to the distorted model improved the correlation, reducing the e.s.d. from 0.304 to 0.150 mT.

In the case of nitrogen having a formal charge of 1, the distorted model secures improved correlation in the one- and two-parameter-cases. Unlike Zeiss and Whitehead,⁵ we were able to parameterise the three-parameter equation (14) for the regular model, although adoption of the distorted model gave a poorer correlation.

TABLE 2

Nitrogen hyperfine couplings: comparison of experimental and calculated values using distorted model

Radical anion	a_N (Experimental)	a_N (Calculated)			
		Equation (12)	Equation (13)	Equation (14)	Equation (15)
$C_6H_5NO_2$	1.395	1.373	1.355	1.340	1.373
2- $FC_6H_4NO_2$	1.415	1.375	1.357	1.344	1.375
3- $FC_6H_4NO_2$	1.330	1.374	1.356	1.341	1.374
3- $FC_6H_4NO_2$	1.228	1.375	1.356	1.346	1.376
C_6H_5CN	0.219	0.228	0.230	0.221	0.246
2- FC_6H_4CN	0.217	0.227	0.229	0.220	0.245
3- FC_6H_4CN	0.226	0.230	0.232	0.222	0.248
4- FC_6H_4CN	0.208	0.229	0.230	0.220	0.245
C_6H_5N	0.631	0.563	0.559	0.560	0.578
2- FC_6H_4N	0.482	0.552	0.548	0.551	0.565
4- $CO_2HC_6H_4N$	0.551	0.530	0.536	0.549	0.559
C_6H_5NH	0.579	0.376	0.591	0.581	0.332

charge of 1, $a_N = 1.721 \rho_N$ (e.s.d. 0.042 mT), $a_N = 1.767 \rho_N - 0.058 \sum_i \rho_{X_i}$ (e.s.d. 0.042 mT), and $a_N = 1.497 \rho_N - 0.321 \sum_i \rho_{X_i} - 0.417 \sum_i \rho_{NX_i}$ (e.s.d. 0.041 mT), respectively.

The feasibility of a Colpa–Bolton type relationship to correlate spin density and hyperfine coupling was investigated [equation (15)] and yielded, for the regular

$$a_N = Q_N^N + K \varepsilon \rho_N \quad (15)$$

model, $a_N = 2.190 \rho_N + 0.345 \varepsilon \rho_N$ (e.s.d. 0.141 mT) and for the distorted case, $a_N = 2.150 \rho_N + 0.702 \varepsilon \rho_N$ (e.s.d. 0.104 mT). The detailed results are compiled in Table 2.

CONCLUSION

In the case of the calculated proton couplings, it is seen that the suggested model effects an improved e.s.d. by some 25% in the correlation expression centred on the simple McConnell relation. Moreover, the additional sophistication of considering nearest-neighbour bond terms is unwarranted and makes little difference to

It is open to question as to whether such a three-parameter scheme has value since, as noted for the proton couplings, increased sophistication is not always justified. For nitrogen having a formal charge of 2, improved correlation is general for the distorted case. An attempt, we believe the first, to fit a Colpa–Bolton-type relationship to the results for nitrogen without regard for the specific formal charge was successful and distortion of the ring improved the fit.

The current work is restricted to π electron calculations, and a desirable extension would take account of σ electrons by application of the INDO method: such an extension is in hand.

We acknowledge the assistance of Dr. D. M. Hirst and Mr. R. Treweek, who assisted with the computer programs. One of us (D. G.) acknowledges the provision of an S.R.C. Post-doctoral Fellowship.

[2/1958 Received, 17th August, 1972]