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THE ELECTRONIC STRUCTURE OF SOME HETEROATOM CONJUGATED COMPOUNDS

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Abstract—Molecular orbital calculations have been carried out on some heteroatom and heterocyclic conjugated compounds. Parameters have been chosen for the coulomb and resonance integrals which lead, in general, to the correctly predicted values of dipole moments, bond lengths and chemical reactivity. The exceptions are azides, oxamide and tetrazole derivatives, and the discrepancies are discussed.

INTRODUCTION

THE simple molecular-orbital method has been shown by Orgel[1] to be a useful means of predicting the electric dipole moments and chemical reactivities in some conjugated heterocyclic compounds. Neglecting overlap, he obtained a set of parameters for the coulomb and resonance integrals which, in general, lead to differences between the predicted and experimental dipole moments of less than 0·3 D for a range of compounds from pyridine to benzoxazole. In all but one of the eighteen compounds considered, the heteroatom was situated within the ring structure, the exception being the "meso ionic" compound Sydnone which had a predicted moment much greater than the experimental value. More recently, Davies[2] has shown that the accuracy of the method is not improved by the inclusion of the overlap integrals.

The study reported here was undertaken with a view to extending the correlation to tetrazole and its derivatives, and to some heteroatom aliphatic compounds. As will appear later, this aim was only achieved in the case of the aliphatic compounds.

PARAMETERS

In the first instance calculations were made using the parameters given in Orgel's paper,[1] but these lead to wrongly predicted dipole moments in simple organic molecules such as ketones, aldehydes and amides. Values for β(CN), β(CO) and β(NO) were therefore adjusted against the dipole moments of cyanides, aldehydes and ketones, and nitromethane respectively. The final choice of parameters is

$$\alpha(\mathrm{C}) = \alpha;\ \alpha(-\mathrm{N}=) = \alpha + \beta;\ \alpha(-\overset{|}{\mathrm{N}}-) = \alpha + 2\beta;$$
$$\alpha(=\mathrm{O}) = \alpha + 2\beta;\ \alpha[\mathrm{C}(-\mathrm{X})] = \alpha + 0{\cdot}1\,\delta\mathrm{X};$$
$$\beta(\mathrm{CC}) = \beta;\ \beta(\mathrm{CN}) = \beta;\ \beta(\mathrm{CO}) = 1{\cdot}8\beta;$$
$$\beta(\mathrm{NN}) = \beta \text{ and } \beta(\mathrm{NO}) = 1{\cdot}2\beta.$$

These values are very similar to those used by Orgel *et al.*[1] and were chosen in preference to those proposed by Brown *et al.*[3,4], since their work was not primarily concerned with dipole moments and consequently their parameters have not been proven for this property.

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[1] L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.* 47, 113 (1951).
[2] D. W. Davies, *Trans. Faraday Soc.* 51, 449 (1955).
[3] R. D. Brown and A. Penfold, *Trans. Faraday Soc.* 53, 397 (1957).
[4] R. D. Brown and M. L. Hefferman, *Trans. Faraday Soc.* 54, 757 (1958).

Following Orgel's work, the dipole moment was calculated by the vector addition of the π moment divided by 1·6 to the σ moment. In all cases the theoretical bond lengths were used and the bond angles taken to be 180°, 60° or those for regular hexagons or pentagons. σ bond moments were estimated using the following individual bond moments.

$$\overset{-}{\mathrm{C}} - \overset{+}{\mathrm{H}} = 0{\cdot}4\,\mathrm{D};\ \overset{-}{\mathrm{N}} - \overset{+}{\mathrm{H}} = 1{\cdot}3\,\mathrm{D};\ \overset{+}{\mathrm{C}} - \overset{-}{\mathrm{N}} = 0{\cdot}45\,\mathrm{D};\ \overset{+}{\mathrm{C}} - \overset{+}{\mathrm{O}} = 0{\cdot}8\,\mathrm{D}$$

$$\overset{+}{\mathrm{N}} - \overset{-}{\mathrm{O}} = 0{\cdot}5\,\mathrm{D}$$

RESULTS

The results are given in Tables 1–3 and Figs. 1 and 2.

Table 1 lists the energies of occupied molecular orbitals [in terms of $(\alpha - \varepsilon)/\beta$] for each compound together with the delocalization energy and, in most cases, the resonance energy. β has been assigned many different values, but a rough value of −20 kcal/mole may be taken for comparative purposes.

TABLE 1. ENERGIES OF THE OCCUPIED MOLECULAR ORBITALS (E_1, E_2 ······)

Compound	E_1	E_2	E_3	E_4	E_5	Delocalization energy	Resonance energy
Alkyl cyanides	1·6466					4·3864 β	0·4 β
Ketones, aldehydes	3·1124					4·0248 β	0·4 β
Carbon dioxide	3·8683	2·0000				10·6732 β	2·6 β
Alkyl cyanates	3·4091	2·0000				8·8724 β	2·6 β
Amides						4·4362 β	0·4 β
Urea	3·6938	2·0000	2·0000			4·7876 β	0·8 β
Oxamide	3·7809	3·1351	2·0000	2·0000		9·0322 β	1·0 β
Glyoxal	3·4439	2·8804				8·2486 β	0·2 β
Azides	2·4142	1·0000				2·8284 β	
Diazomethane	2·2582	2·0000	0·5912			4·5988 β	0·6 β
Nitromethane	3·6971	2·0000				3·3942 β	
Nitrate ion	3·7321	2·0000				3·4642 β	
Guanidine	3·0000	2·0000	1·2808			3·0616 β	0·9 β
Nitroguanidine imino	3·9100	2·9590	2·0000	2·0000	1·4399	7·1378 β	
amino	4·0257	2·8962	2·0000	2·0000	1·3063	6·9564 β	
Dicyandiamide imino	3·0407 2·0697	2·0599 1·0000	2·0000	1·1529		8·7464 β	2·2 β
amino	3·1627 2·0697	2·3173 1·0000	1·5144	1·2367		9·5016 β	2·9 β
Pyrrole	2·9131	1·2643	0·7662			5·4872 β	1·5 β
Pyridine	2·3132	1·3188	1·0512			8·1664 β	2·1 β
Aniline	2·6578	1·7920	1·0000	0·8017		8·3030	2·3 β
Tetrazole 1 1-Ethyltetrazole 1,5-Dimethyltetrazole	3·2015	2·0000	1·3907			5·8844 β	1·7 β
Tetrazole 2 2-Ethyltetrazole	3·2407	1·8330	1·4456			5·8386 β	1·6 β
1-Ethyl-5-ethylamino-tetrazole	3·3500	2·3698	2·0000	1·1654		6·2704 β	2·1 β
2-Methyl-5-methylamino-tetrazole	3·32075	2·5305	1·7532	1·1904		6·1897 β	2·0 β
1,3-Dimethyl-5-imino-tetrazole	3·4582	3·4222	1·8705	0·8635		7·3288 β	
1,4-Dimethyl-5-imino-tetrazole	3·4644	2·4142	1·8800	1·0000		7·6172 β	3·4 β

Fig. 1 contains diagrams of the electron densities on each atom, and the mobile bond order for each bond in all the non-cyclic structure studies. Comparison of the theoretical and experimental bond lengths[5] in these compounds is given underneath

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[5] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Special Publication No. 11 of the Chemical Society, London (1958).

the diagram of each molecule, the theoretical bond lengths being interpolated from graphs of single, double and triple covalent bond lengths[6] against mobile bond order. Although there is some doubt in defining pure C—N double bonds, bond lengths are relatively insensitive to changes in parameters and Coulson[7] has pointed out that the simplest molecular orbital method gives results which are as reliable as those given by the more refined treatments. Comparison of the predicted and observed dipole moments of the non-cyclic compounds is given in Table 2. Unless otherwise stated, the observed dipole moments have been taken from Wesson's compilation.[8]

Fig. 2 and Table 3 contain similar results for the cyclic compounds.

TABLE 2. PREDICTED AND EXPERIMENTAL DIPOLE MOMENTS OF SOME HETEROATOM CONJUGATED COMPOUNDS

Compound	π Moment calculated	σ Moment predicted	Total moment predicted	Total moment observed
Alkyl cyanides	4·5	0·85	3·7	3·6
Aldehydes, ketones	2·6	1·2	2·9	2·6–2·9
Alkyl amides	3·6	1·5	3·7	3·5
	$\theta = 76°$	$\theta = 75°$	$\theta = 76°$	
Urea	4·3	1·7	4·4	4·6
Alkyl azides	0·3	0·85	0·80	1·6
		$\theta = 60°$	$\theta = 72°$	
Diazomethane	1·2	0·85	1·6	1·4
Nitromethane	3·5	1·4	3·6	3·5
Nitroguanidine imino	11·2	1·8	8·3	7·0
	$\theta = -31·5°$	$\theta = -14°$	$\theta = -29°$	
amino	15·3	1·7	11·1	
	$\theta = -20°$	$\theta = -54°$	$\theta = -23°$	
Dicyandiamide imino	14·2	1·5	9·8	—
	$\theta = -40°$		$\theta = 34°$	
amino	8·8	1·0	6·0	—
	$\theta = 28°$	$\theta = 90°$	$\theta = 36°$	

θ is measured anticlockwise, relative to a $L \rightarrow R$ horizontal axis in the charge diagrams.

DISCUSSION

The discussion can be conveniently divided into two parts, the first dealing with the non-cyclic compounds, and the second with the cyclic ones.

Non-cyclic molecules

Agreement between the predicted and experimental bond lengths (Fig. 1) and dipole moments (Table 2) is good. In general, it is within 0·02 Å for bond lengths and 0·2 D for dipole moments. However, there are a few exceptions which merit special comment, namely azides, oxamide, nitroguanidine and dicyandiamide.

Azides

Although the theoretical bond lengths agree well with the experimental value, the predicted dipole moment is too small. Bonnemay and Daudel[9] have however shown

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[6] G. W. Wheland, *Resonance in Organic Chemistry* p. 172. John Wiley, New York (1955).

[7] C. A. Coulson, *Theoretical Organic Chemistry* p. 54. Chemical Society Kekulé Symposium, Butterworths, London (1959).

[8] L. G. Wesson, *Tables of Electric Dipole Moments.* Technology Press, Massachusetts Institute of Technology (1948).

[9] A. Bonnemay and R. Daudel, *C.R. Acad. Sci., Paris* **230**, 2300 (1950).

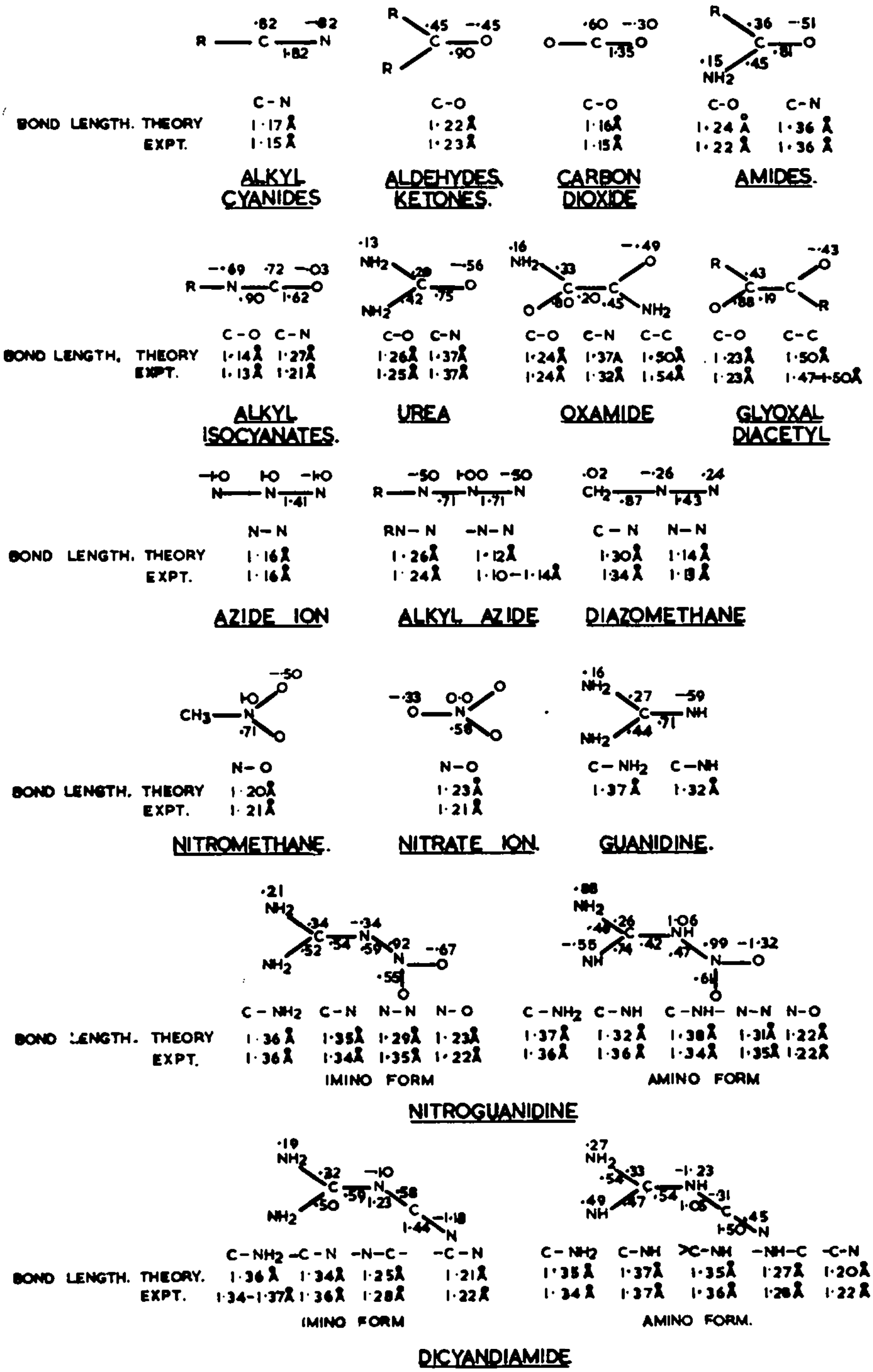
R C N ·82 −·82 1·82
R R C O ·45 −·45 ·90
O C O ·60 −·30 1·35
R C O NH2 ·36 −·51 ·15 ·45 ·81
BOND LENGTH. THEORY
EXPT.
C-N 1·17Å 1·15Å
C-O 1·22Å 1·23Å
C-O 1·16Å 1·15Å
C-O 1·24Å 1·22Å C-N 1·36Å 1·36Å
ALKYL CYANIDES
ALDEHYDES. KETONES.
CARBON DIOXIDE
AMIDES.
R N C O −·69 ·72 −·03 ·90 1·62
NH2 NH2 C O ·13 ·29 −·56 ·42 ·75
NH2 C C O O NH2 ·16 ·33 −·49 ·80 ·20 ·45
R C C O O R ·43 −·43 ·88 ·19
BOND LENGTH, THEORY
EXPT.
C-O 1·14Å 1·13Å C-N 1·27Å 1·21Å
C-O 1·26Å 1·25Å C-N 1·37Å 1·37Å
C-O 1·24Å 1·24Å C-N 1·37A 1·32Å C-C 1·50Å 1·54Å
C-O 1·23Å 1·23Å C-C 1·50Å 1·47–1·50Å
ALKYL ISOCYANATES.
UREA
OXAMIDE
GLYOXAL DIACETYL
N N N −1·0 1·0 −1·0 1·41
R N N N −·50 1·00 −·50 ·71 1·71
CH2 N N ·02 −·26 ·24 ·87 1·43
BOND LENGTH. THEORY
EXPT.
N-N 1·16Å 1·16Å
RN-N 1·26Å 1·24Å -N-N 1·12Å 1·10–1·14Å
C-N 1·30Å 1·34Å N-N 1·14Å 1·13Å
AZIDE ION
ALKYL AZIDE
DIAZOMETHANE
CH3 N O O −·50 1·0 ·71
O N O O −·33 0·0 ·58
NH2 NH2 C NH ·16 ·27 −·59 ·44 ·71
BOND LENGTH. THEORY
EXPT.
N-O 1·20Å 1·21Å
N-O 1·23Å 1·21Å
C-NH2 1·37Å C-NH 1·32Å
NITROMETHANE.
NITRATE ION.
GUANIDINE.
NH2 NH2 C N N O O ·21 ·34 −·34 ·52 ·54 ·59 ·92 −·67 ·55
NH2 NH C NH N O O ·88 ·48 ·26 1·06 −·55 ·74 ·42 ·47 ·99 −1·32 ·64
BOND LENGTH. THEORY
EXPT.
C-NH2 1·36Å 1·36Å C-N 1·35Å 1·34Å N-N 1·29Å 1·35Å N-O 1·23Å 1·22Å
IMINO FORM
C-NH2 1·37Å 1·36Å C-NH 1·32Å 1·36Å C-NH- 1·38Å 1·34Å N-N 1·31Å 1·35Å N-O 1·22Å 1·22Å
AMINO FORM
NITROGUANIDINE
NH2 NH2 C N C N ·19 ·32 −·10 ·50 ·59 1·23 ·58 −1·18 1·44
NH2 NH C NH C N ·27 ·54 ·33 −1·23 ·49 ·47 ·54 1·06 −·31 ·45 1·50
BOND LENGTH. THEORY.
EXPT.
C-NH2 1·36Å 1·34–1·37Å -C-N 1·34Å 1·36Å -N-C- 1·25Å 1·28Å -C-N 1·21Å 1·22Å
IMINO FORM
C-NH2 1·35Å 1·34Å C-NH 1·37Å 1·37Å >C-NH 1·35Å 1·36Å -NH-C 1·27Å 1·28Å -C-N 1·20Å 1·22Å
AMINO FORM.
DICYANDIAMIDE

FIG. 1.

TABLE 3. PREDICTED AND EXPERIMENTAL DIPOLE MOMENTS IN SOME HETEROCYCLIC CONJUGATED COMPOUNDS

Compound	π Moment calculated	σ Moment predicted	Total moment predicted	Total moment observed
Tetrazole (1)*	4·7	1·8	4·8	5·1
	$\theta = 54°$	$\theta = 43°$	$\theta = 50°$	
(2)*	2·4	0·77	2·15	
	$\theta = 134°$	$\theta = 99°$	$\theta = 122°$	
1-Ethyltetrazole	4·7	1·4	4·4	5·5
1,5-Dimethyltetrazole	$\theta = 54°$	$\theta = 34°$	$\theta = 49°$	5·3
2-Ethyltetrazole	2·4	0·56	1·8	2·7
	$\theta = 134°$	$\theta = 64°$	$\theta = 118°$	
1-Ethyl-5-ethylamino-tetrazole†	5·6	1·6	5·1	7·4
	$\theta = 42°$	$\theta = 49°$	$\theta = 44°$	
	5·6	1·1	5·0	
	$\theta = 42°$	$\theta = 20°$	$\theta = 37°$	
5-Aminotetrazole (1)*	5·6	1·9	5·4	5·7
		$\theta = 42°$	$\theta = 42°$	
2-Methyl-5-methylamino-tetrazole†	1·6	0·9	1·9	2·55
	$\theta = 107°$	$\theta = 82°$	$\theta = 95°$	
1·3-Dimethyl-5-iminotetrazole	10·1	0·9	5·4	4·0
	$\theta = 110°$	$\theta = 276°$	$\theta = 112°$	
1·4-Dimethyl-5-iminotetrazole	4·5	−1·1	1·7	1·7
Pyrrole	2·0	0·3	1·6	1·8
Pyridine	2·3	0·85	2·3	2·2
Aniline	0·9	1·2	1·7	1·6

* Hydrogen in 1 or 2 position.
† σ moment depends on the stereochemistry of the 5-alkylamino group.
θ is measured anticlockwise relative to an upward vertical axis in the charge diagrams.

that a more complete treatment leads to accurately predicted bond lengths, and using their values for the electron densities, the π moment becomes 2·3 D giving a total predicted moment of 1·3 D, $\theta = 144°$ in good agreement with the experimental value of 1·6 D found in phenyl azide.

Oxamide

The bond lengths in oxamide[10,11] and other compounds of this general type, i.e. dithiooxamide,[12] oxalic acid,[13] and parabanic acid,[14] have been thoroughly examined and the central carbon–carbon bond length shown to be 1·5 Å, i.e. a pure single bond. Since all the compounds are planar or mainly planar and the bond angles at the carbon atoms consistent with trigonal hybridisation, complete delocalization over the entire σ bond structure (other than X—H bonds) would be expected, and calculations suggest that the carbon–carbon distance should be shortened by 0·05 Å. Poor agreement is also obtained for the carbon nitrogen bonds which are considerably shorter than the predicted value. If, however, the amino groups in oxamide are replaced by hydrogen (glyoxal), methyl groups (diacetyl) or chlorine (oxalyl chloride), the central

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[10] E. M. Ayerst and J. R. C. Duke, *Acta Cryst.* **7**, 588 (1954).
[11] C. Romers, *Acta Cryst.* **6**, 429 (1953).
[12] B. Long, P. Markey and P. J. Wheatley, *Acta Cryst.* **7**, 140 (1954).
[13] K. G. Cox, M. W. Daugell and G. A. Jeffrey, *J. Chem. Soc.* 4854 (1952).
[14] D. R. Davies and J. J. Blum, *Nature, Lond.* **173**, 993 (1954): *Acta Cryst.* **8**, 129 (1955).

carbon–carbon bond distance is shortened by about 0·07 Å and agreement between experiment and theory is good (see Fig. 1). Similarly the corresponding carbon–carbon bond distances in the more complicated molecules dimethyl glyoxime, furoic acid, 6-carbomoyl 3 pyridazone and isatin lies between 1·44 Å and 1·49 Å. At first sight it might be thought that the phenomenon is caused by the repulsion of the adjacent positive charges of +0·33 electrons on the carbon atoms in oxamide. This is unlikely since the repulsive forces would be even greater in molecules of the glyoxal type where the adjacent charges are +0·43 electrons. Obviously important intramolecular forces must be acting between the heteroatoms in the oxamide type of molecules which are not present in the glyoxal type and which have not been included in the simple molecular orbital treatment. These forces probably involve hydrogen bonds, but the nature of the bonding is obscure and outside the scope of the present paper.

Nitroguanidine

Doubt existed for some time as to whether nitroguanidine existed in the imino or amino form, and the problem was only recently resolved by Richards and Yorke[15] who examined its nuclear magnetic resonance proton spectra and showed that the solid existed in the imino form. The theoretical bond lengths give a better fit with the experimental values[16] for the imino form, especially around the guanyl part of the molecular. In benzene solution, the reasonably close approach of the predicted dipole moment of the imino form (8·3 D) to the experiment moment (6·95 D),[17] and the greater delocalization energy of the imino form (7·1378 β) as compared with the amino form (6·9564 β) indicates the former structure to be more stable in solution.

Dicyandiamide

Whereas the imino structure is shown to be the more stable form of nitroguanidine, the amino form appears to be more stable in the case of dicyandiamide. The delocalization energy is greater for the amino form (9·5016 β) than the imino form (8·7464 β), and better agreement is obtained between the theoretical and experimental bond lengths[18] with the amino form. In the past it has been assumed[19] that difference in the terminal C—NH or C—NH_2 bond lengths was due to experimental error, but this does not appear to be so. No experimental dipole moment data is available for confirmatory purposes.

Cyclic molecules

In the molecular orbital calculations of heterocyclic nitrogen compounds the parameters chosen were those used by Orgel,[1] with the exception of β(CN) which was equated to β rather than 1·2 β. This change does not appear to alter the accuracy of the results for carbon-nitrogen heterocyclics. Calculations on pyridine and pyrrole lead to predicted dipole moments agreeing to within 0·1 D of the experimental value, and calculations on 1-ethyltetrazole and 2-ethyltetrazole using $\beta(CN) = \beta$ and $\beta(CN) = 1{\cdot}2\ \beta$ gave predicted dipole moments which did not differ by more than 0·05 D in each respective case. For aniline, the agreement between the predicted and

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[15] R. E. Richards and R. W. Yorke, *Trans. Faraday Soc.* **54**, 321 (1958).

[16] J. H. Bryden, L. A. Burkardt, E. W. Hughes and J. Donohue, *Acta Cryst.* **9**, 573 (1956).

[17] W. D. Kumler and P. P. T. Sah, *J. Org. Chem.* **18**, 629 (1954).

[18] E. W. Hughes, *J. Amer. Chem. Soc.* **62**, 1258 (1940).

[19] Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules and the Chemical Bond* p. 184. Butterworths, London (1950).

experimental dipole moment shows that the chosen parameters are also valid for aromatic compounds containing an amino group attached to the ring structure.

In view of the good agreement between theory and experiment obtained both in Orgel's work and the present results, it was surprising to find that the predicted dipole moments of tetrazole or its derivatives, in general did not agree with the experimentally measured moments.[20,21] Even in those cases in which agreement appears to be good, i.e. tetrazole-1(H), 5-aminotetrazole-1(H) and 1,4-dimethyl 5-aminotetrazole, it is believed that the agreement is fortuitous. In tetrazole and 5 aminotetrazole both tautomerism and hydrogen bonding is possible. Problems arising in this way are usually resolved by studying the alkyl derivatives. Predicted values of the dipole moments of 1-ethyl- and 2-ethyl-tetrazole are 4·4 D and 1·8 D respectively and bear little resemblance to the experimentally measured values of 5·5 D and 2·7 D respectively. Replacing the ethyl groups by a hydrogen atom increases the predicted dipole moment by 0·4 D in each case, whereas the observed moment is 0·4 D *lower* than the value for 1-ethyltetrazole. The experimental values for tetrazole and 5-aminotetrazole were measured in dioxan[21] and the results of the present calculations suggest that these

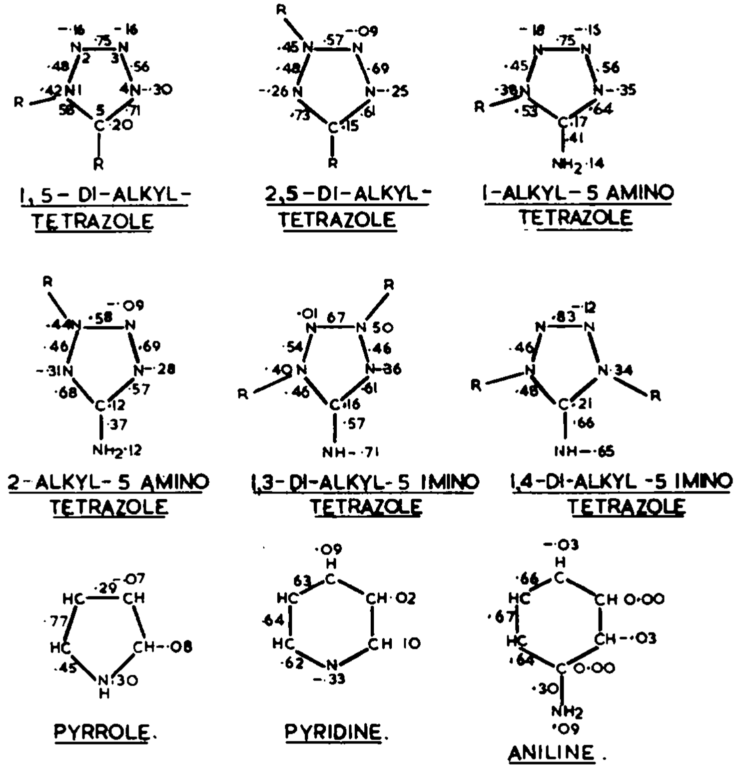

Fig. 2.

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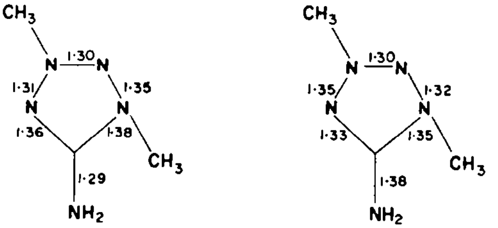
[20] M. H. Kaufman, F. M. Ernsberger and W. S. McEwen, *J. Amer. Chem. Soc.* **78**, 4197 (1956).

[21] K. A. Jensen and A. Friediger, *Kgl. Danske Videnskab Selskab, Math-fys Medd.* **20**, No. 20, 1 (1943).

compounds in this solvent exist as tautomers. A simple calculation based on the experimental dipole moments indicates an approximate 70:30 ratio of the 1(H) to the 2(H) tautomers.

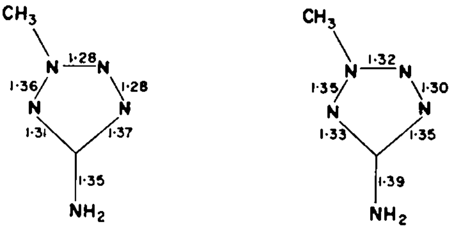
Attempts to clarify the situation by a study of the nuclear magnetic resonance proton spectra have not been successful.[22] Tetrazole is only sparingly soluble in dioxan and benzene and NMR peaks were only obtained in dimethyl formamide and in sulphuric acid. Unfortunately these solvents affect tetrazole chemically. In the proton accepting solvent dimethyl formamide, tetrazole dissociates, and the n.m.r. spectra shows only a single peak, apart from the solvent peaks, at —3·27 p.p.m. presumably due to the CH proton. Conversely, in 100 per cent sulphuric acid at least two or more of the tetrazole nitrogens would be protonated giving rise to further difficulties in interpretation of the spectrum.

Comparison of the bond lengths in the tetrazole derivatives is only possible in two cases. With the meso ionic compounds 1·3 dimethyl 5-aminotetrazole[23] agreement is poor and the short C—NH$_2$ bond length found experimentally strongly suggests that the compound is in the imino (C—NH) form. In the other case 2-methyl 5-aminotetrazole[20] agreement is good.



Experiment Theory

1,3-dimethyl-5-amino tetrazole



Experiment Theory

2-methyl-5-amino tetrazole

It is interesting to note that the simple molecular orbital theory predicts wrong dipole moments for azides as well as tetrazoles, and suggests that the values of β(NN) used in the calculations were inaccurate. However, calculations carried out using different values of β(NN) did not improve the agreement in the case of tetrazoles.

[22] R. G. Kidd and B. Figgis, Private communication (1960).

[23] J. H. Bryden, *Acta Cryst.* **8**, 211 (1955).

CONCLUSIONS

The simple molecular orbital theory leads to results which correctly predict the dipole moments, chemical reactivity and bond lengths in a large number of heterocyclic (see ref. 1) and heteroatom conjugated compounds. Tetrazole derivatives, tetrazole, azides and oxamide appear to be exceptions to the rule. In some cases hydrogen bonding may be the cause of the discrepancy.

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