

TABLE 2

MOLECULE	RADIUS SUM	OBSERVED DISTANCE	MOLECULE	RADIUS SUM	OBSERVED DISTANCE
ICl	I:Cl = 2.32 Å	2.31 Å			
HCl	H:Cl = 1.28	1.28	O ₂ ¹ Σ	O::O = 1.18 Å	1.22 Å
HBr	H:Br = 1.43	1.42	H ₂ CO	C::O = 1.28	1.25
HI	H:I = 1.62	1.62			
H ₂ O	O:H = 0.95	0.94*	N ₂	N:::N = 1.10	1.10
NH ₃	N:H = 0.99	0.98*	HCN	C:::N = 1.16	1.16†
CH ₄	C:H = 1.06	1.08**	CN	C:::N = 1.16	1.17
CH ₃ F	C:F = 1.41	1.43*	C ₂ H ₂	C:::C = 1.22	1.21‡‡

* From R. Mecke, "Leipziger Vorträge 1931."

** R. G. Dickinson, R. T. Dillon and F. Rasetti, *Phys. Rev.*, **34**, 582 (1929).

† R. M. Badger and J. L. Binder, *Ibid.*, **37**, 800 (1931).

‡‡ From $I = 23.509 \times 10^{-40}$ g./cm.² (R. Mecke, *Z. Elektrochem.*, **36**, 803 (1930)) assuming C:H = 1.06 Å.

The comparison of radius sums and observed interatomic distances from band-spectral data given in table 2 shows agreement in general to within about 0.02 Å.

Often two or more reasonable Lewis formulas for a molecule can be written and until recently it has not been possible to reach a confident decision regarding the correct electronic structure in such a case. The comparison of observed interatomic distances with radius sums from table 1 provides considerable information on this point. For example, the two structures :C::O: and :C:::O: for the normal state of carbon monoxide correspond to the interatomic distances 1.28 Å and 1.13 Å, respectively, so that the observed distance 1.15 Å eliminates the first and supports the second. I have recently shown¹ by the study of energy curves, however, that the normal state of the molecule resonates between these two structures, with the triple-bonded structure somewhat more important than the other. Because of the additional energy provided by this resonance, we expect the bond to be stronger than the average for the two structures, and the equilibrium interatomic distance to be smaller than the mean of 1.28 and 1.13 Å. The observed value indicates that *resonance between two or more structures leads to interatomic distances nearly as small as the smallest of those for the individual structures.*

Further support of this is provided by nitrous oxide. The linear configuration NNO with the oxygen atom at one end is supported by the kernel repulsion rule² and much chemical evidence, and evidence convincing to physicists has recently been obtained in a band-spectral investigation,³ which also provided the value $I = 59.4 \times 10^{-40}$ g./cm.² for the moment of inertia. Now the usually written electronic structure :N::N::O:, with distances N—N = 1.26 and N—O = 1.22 Å, leads to $I = 75.8 \times 10^{-40}$,

and so cannot be correct. A consideration of the energy relations involved indicates $\text{:N}::\text{N}:\ddot{\text{O}}:$ and $\ddot{\text{N}}:\text{N}::\text{O}:$ to be about as stable as the double-bonded structure. These give $I = 75.3$ and 75.2×10^{-40} , respectively. Combining the first and second structures and assuming the N—N and N—O distances to be 1.10 and 1.22 Å, the still unsatisfactory value 66.7 Å is obtained. But the distances $\text{N}::\text{N} = 1.10$ Å and $\text{N}::\text{O} = 1.07$ Å lead to $I = 58.1 \times 10^{-40}$ g./cm.², in excellent agreement with observation. This corresponds to resonance among the three structures listed above (provided the structure $\ddot{\text{N}}:\text{N}::\ddot{\text{O}}:$ is included at all), with each interatomic distance equal to the smallest of the values predicted by the various structures. *Both the N—N and the N—O bond behave like triple bonds.*

A rough value $I = 70 \times 10^{-40}$ for carbon dioxide from Raman spectra⁴ leads to a carbon-oxygen distance of about 1.15 Å. The structure $\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$ gives $\text{C}::\text{O} = 1.28$ Å, and so is not correct. But if the molecule resonates between this structure and the two other reasonable ones $\ddot{\text{O}}:\text{C}::\ddot{\text{O}}:$ and $\ddot{\text{O}}::\text{C}:\ddot{\text{O}}:$ the carbon atom would be about 1.13 Å from each oxygen atom.

The observed average distances 1.15 ± 0.05 Å for N_3^- and NCO^- in crystals show that these ions, isosteric with CO_2 and N_2O , also resonate among these three electronic structures.

The value of the carbon-carbon distance in graphite (1.42 Å) and in benzene (1.42 ± 0.03 Å in $\text{C}_6(\text{CH}_3)_6$) indicates strongly that the bonds are not single bonds (1.54 Å) but are resonating between single and double bonds (1.38 Å), as in the Kekulé structure. No indication is provided as to whether or not other electronic structures contribute significantly to the benzene structure. In the graphite-like crystal BN each B is surrounded by three N's at 1.45 Å, and in the molecule $\text{B}_3\text{N}_3\text{H}_6$, with an atomic configuration like that of benzene, the B—N distance⁵ is 1.47 ± 0.07 Å. These values eliminate structures involving single B—N bonds only (1.59 Å), and support resonance between single and double bonds (1.43 Å), as in the carbon compounds.

In many other molecules and ions resonance among several equivalent structures occurs. In CO_3^- and NO_3^- there are three structures of the

type $\ddot{\text{O}}:\text{C}::\ddot{\text{O}}:$ differing only in the choice of the double-bonded oxygen. The observed C—O and N—O distances of 1.25 ± 0.04 Å ($\text{C}:\text{O} = 1.43$, $\text{C}::\text{O} = 1.28$, $\text{N}:\text{O} = 1.36$, $\text{N}::\text{O} = 1.22$ Å) indicate the importance of the double bond and of resonance energy in reducing interatomic dis-

tances. The amount of contribution of ionic structures to the normal states of these ions is unknown.

The existence of resonance among several electronic structures leads to direct explanations of many chemical properties of molecules, such as, for example, the acid properties of the carboxyl group as compared with

the hydroxyl group. The structures $\text{R}:\overset{\cdot\cdot}{\text{C}}:\overset{\cdot\cdot}{\text{O}}:\text{H}$ and $\text{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\overset{\cdot\cdot}{\text{O}}:\text{H}$ do not sug-

gest that any difference in the oxygen-hydrogen bond should exist. But the carboxyl group actually resonates between this structure and the structure $\text{R}:\overset{\cdot\cdot}{\text{C}}::\overset{\cdot\cdot}{\text{O}}:\text{H}$, so that the hydrogen atom is attached to an oxy-

gen atom which forms a double bond with carbon half the time, in consequence of which ionization takes place easily. Resonance involving double bonds also affects the tendency of a molecule to take up hydrogen

ions. The aliphatic amines, $\text{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$, tend to add a proton to the unshared electron pair of the nitrogen atom. They are accordingly strong bases, forming salts with mineral acids, and they also form complexes with gold, platinum and mercury, the unshared pair forming the bond with the metal atom. In the amides, on the other hand, resonating be-

tween the structures $\text{R}:\overset{\cdot\cdot}{\text{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$ and $\text{R}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\overset{\cdot\cdot}{\text{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$, there is no unshared

electron pair on the nitrogen atom (although one pair is shared only part of the time), and in consequence these substances are not basic, but have faintly acid properties. Hydrazine, N_2H_4 and the diamines, such as ethylene diamine, $\text{C}_2\text{H}_4(\text{NH}_2)_2$, are di-acid bases, since each NH_2 group can take up one proton. But urea, $\text{CO}(\text{NH}_2)_2$, is only a mono-acid base, and the proton is added to oxygen rather than nitrogen, for resonance

among the structures $\text{H}:\overset{\cdot\cdot}{\text{N}}:\overset{\cdot\cdot}{\text{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$, $\text{H}:\overset{\cdot\cdot}{\text{N}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\overset{\cdot\cdot}{\text{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$ and $\text{H}:\overset{\cdot\cdot}{\text{N}}:\overset{\cdot\cdot}{\text{C}}::\overset{\cdot\cdot}{\text{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\text{:H}$ leaves

unshared pairs on the oxygen atom alone, and, moreover, gives the oxygen atom greater proton affinity than ketonic oxygen. The amidines, RC.NH.NH_2 , and guanidines, $\text{C.NH}(\text{NH}_2)_2$, are mono-acid bases, the

resonance-migration of the double bond permitting only NH to add a proton.

¹ Linus Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).

² Linus Pauling and S. B. Hendricks, *Ibid.*, **48**, 641 (1926).

³ E. K. Plyler and E. F. Barker, *Phys. Rev.*, **38**, 1827 (1931).

⁴ W. V. Houston and C. M. Lewis, *Ibid.*, **37**, 227 (1931).

⁵ A. Stock and R. Wierl, *Z. anal. Chem.*, **203**, 228 (1931).

THE PENETRATION OF 1-NAPHTHOL-2-SULPHONATE INDOPHENOL, O-CHLORO PHENOL INDOPHENOL AND O-CRESOL INDOPHENOL INTO SPECIES OF VALONIA FROM THE SOUTH SEAS

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The purpose of this investigation was to see whether the oxidation-reduction indicators penetrate other species of *Valonia* in the same way as they do those already investigated.

The species used in these studies were found in the South Seas, namely, *V. ventricosa*, *V. forbesii* and *V. fastigiata*.¹ The dyes used were 1-naphthol-2-sulphonate indophenol, *o*-chloro phenol indophenol and *o*-cresol indophenol. These were dissolved in sea water in a concentration of 0.000097 M. The sea water was buffered with phosphate or borate buffers producing pH values of from 6.3 to 8.1, according to the H electrode. The plants were allowed to remain in these solutions for various lengths of time up to 12 hours or more at a temperature of from 25° to 27°C. At intervals plants were taken out and the sap expressed. The dye was always found in the sap in a reduced form (colorless). The color was brought back by adding a trace of NaOH. The concentration of dye in the sap was measured by comparison with solutions of dye of known concentrations in like-sized tubes. No evidence of injury was noted, such as changes in microscopic or macroscopic appearance or subsequent survival.

It was found that 1-naphthol-2-sulphonate indophenol did not penetrate at any pH value of the external solution used. The remaining two dyes penetrated into the sap in a colorless form. The rate of penetration was dependent in these experiments upon the pH value of the external solution. Penetration was faster from the more acid solutions, decreasing as the sea water became more alkaline. When either of these two dyes came to