

The Mo's ψ_i are linear combinations between ligand- and Fe metal-orbitals. Combining relations are decided by the symmetry D_{5h} of the molecule. Electron repulsion integrals are neglected except $\gamma_{rs} = \int \phi_r^2(1)\phi_s^2(2)(1/r_{12})dv_1dv_2$. Only one- and two-center type integrals are considered. The tables of Kotani *et al.*,⁵ Roothaan,⁶ and Rudenberg⁷ are used. The resonance integral $\beta_{rs} = \int \phi_r | - | \phi_s dv$ is neglected except first neighbors. The β for C-C neighbors has been given the value suggested by Pariser and Parr⁸ for benzene, namely, $\beta_{C-C} = -2.39$ eV, and the ones for Fe-C neighbors are assumed to be proportional to the overlap integrals.⁹ Two structures are considered separately.

(a) When one ring is a reflection of the other by the horizontal plane: the direction combining two centers of ring is written as the x -axis, and the one through the position 5⁽¹¹⁾ of C is written as the y -axis. Then ligand- and metal-orbitals are combined as follows:

$$(a_2'')\alpha\rho_0^+ + \beta\phi_x; (a_1')\alpha\rho_0^- + \beta\phi_x + \gamma\phi_{(x^2-y^2)}; \\ (e_1')\alpha\rho_1^- + \beta\phi_y; \alpha\rho_{-1}^- + \beta\phi_x; (e_2')\alpha\rho_2^- + \beta\phi_{(y^2-z^2)}; \alpha\rho_{-2}^- \\ + \beta\phi_{yz}; (e_1'')\alpha\rho_1^+ + \beta\phi_{yz}; \alpha\rho_{-1}^+ + \beta\phi_{xz}; (e_2'')\rho_2^+; \rho_{-2}^+.$$

The MO energies obtained are -15.45 eV (a_2''), -5.88 eV ($a_2''^*$), -16.80 eV (a_1'), -8.57 eV ($a_1'^*$), -7.07 eV ($a_1''^*$), -7.68 eV (e_1'), -3.99 eV ($e_1'^*$), -7.87 eV (e_2'), -3.64 eV ($e_2'^*$), -8.90 eV (e_1''), -5.28 eV ($e_1''^*$), and -3.68 eV (e_2'').

(b) When one ring is an inversion of the other by the center of molecule: for symmetries a_1' , a_2'' , e_2'' MO's are the same as (a); for symmetries e_1' , e_2' , e_1'' there are interactions between, for example, ρ_1^- , ϕ_y and ρ_{-1}^- , ϕ_x , but when from doubly degenerated orbitals ρ_1'' , ρ_{-1}'' we make a new set of orbitals $\bar{\rho}_1''$, $\bar{\rho}_{-1}''$, it proves that $\bar{\rho}_1''$ combines only with ϕ_y and $\bar{\rho}_{-1}''$ only with ϕ_x . The results are the same as (a).

The ground state has the closed shell configuration $A:(a_1')^2(a_2'')^2(e_1'')^4(a_1'^*)^2(e_2'')^4(e_1')^4$, and the Fe-C bonding is 33% ionic, 67% homopolar on the average.

Next, only singly excited states are considered for transitions. As the dipole moments of the molecule M_x , M_y , M_z belong to symmetries A_2'' , E_1' , E_1' , respectively, there exist 10 allowed transitions from the ground state. Without CI the transition energies to low excitation levels are 0.9 eV, 3.8 eV ($A_1' \rightarrow E_1'$); 2.5 eV, 3.7 eV ($A_1' \rightarrow A_2''$).

¹ E. A. Seibold and L. E. Sutton, *J. Chem. Phys.* **23**, 1967 (1955).

² Wilkinson, Rosenblum, Whiting, and Woodward, *J. Am. Chem. Soc.* **74**, 2125 (1952).

³ C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951).

⁴ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

⁵ Kotani, Amemiya, Ishiguro, and Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., 1955).

⁶ C. C. J. Roothaan, *J. Chem. Phys.* **19**, 1445 (1951).

⁷ K. Rudenberg, *J. Chem. Phys.* **19**, 1459 (1951).

⁸ R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 767 (1953).

⁹ Mulliken, Rieke, Orloff, and Orloff, *J. Chem. Phys.* **17**, 1248 (1949).

Simultaneous Light-Absorption and Emission Measurements behind a Shock Wave*

F. HARSHBARGER

Daniel and Florence Guggenheim Jet Propulsion Center,
California Institute of Technology, Pasadena, California

(Received April 4, 1956)

IN connection with current extensive studies on the rate of carbon formation behind weak shocks in acetylene, it proved to be desirable to obtain simultaneous light-absorption and emission data. The absorption experiments are complicated because of intense emitted radiation associated with chemical reaction behind the shock front. One method for separating the emitted component from the transmitted light involves the use of carefully matched photocells and subtracting the emitted radiation from the sum of the transmitted and emitted radiation.¹ Another method involves the use of chopped light for the absorption measurements. However, the chopping rate places an upper limit on the rates of reaction that can be studied. A Kerr cell² using

nitrobenzene can be used to modulate the light at frequencies greater than 10 megacycles without appreciable attenuation and is therefore suitable for the study of reaction rates behind weak shocks.

The use of a Kerr cell³ made it possible to study simultaneously emission and absorption during the decomposition of acetylene behind weak shocks. The light source was a General Electric Type 524 xenon lamp, with a peak intensity of 50 million lumens when pulsed for 1 millisecond. This lamp was operated so that its peak radiation lasted about 400 microseconds. The lamp was fired by discharging a capacitor through a thyratron tube which was suitably delayed so that the peak intensity of the xenon source occurred during the time that the shock passed the observation station in the shock tube. The light from the xenon source passed through the Kerr cell and then through the shock tube. Both the emitted light and the transmitted modulated light (with or without the use of a suitable monochromator) may be detected on a single photomultiplier tube whose output is then displayed on an oscilloscope. The ac component of the phototube output represents the transmitted light, the dc component corresponds directly to the emitted light.⁴

Another possible use of the Kerr cell involves the use of a Kerr-cell modulated prism as beam deviator followed by a monochromator.⁵ This combination may be used as a high-speed scanning monochromator with time resolution sufficient for studies behind weak shocks.

It is felt that the successful development of new high-speed recording and scanning devices will facilitate full utilization of the potentials of the shock tube for quantitative high-temperature gas dynamic investigations.

* Work supported by the Office of Naval Research under Contract Nonr-220(03), NR 015 401 and by the U. S. Air Force Office for Scientific Research under Contract AF 18(603)-2. The author is indebted to Dr. S. S. Penner for helpful discussions.

¹ Experiments of this type have been carried out by Mr. W. Hooker of our staff while he was associated with the General Electric Company.

² The use of the Kerr cell was suggested by Dr. N. Davidson.

³ The author is indebted to Dr. A. Ellis for the use of his Kerr cell.

⁴ This arrangement permits several obvious extensions. For example, the emitted radiation in several distinct wavelength regions can be chopped at different frequencies and recorded simultaneously on a single photoelectric receiver.

⁵ This method of approach was suggested by Dr. S. S. Penner and has been studied by Dr. V. Vali of the Lockheed Aircraft Company.

Comparison of Infrared and Cryoscopic Studies of Solutions of Pyrrole in Nonpolar Solvents. Formation of Polymers*

MARIE-LOUISE JOSIEN, PAUL PINEAU, AND MARCEL PATY,
Faculté des Sciences, Bordeaux, France.

AND

NELSON FUSON, *Fisk University, Nashville, Tennessee*
(Received April 13, 1956)

EXAMINATION of the infrared spectra of pyrrole in medium concentrations in carbon tetrachloride¹ enables one to distinguish two bands attributed to the stretching vibration of the NH group. Of the two, the sharper, higher frequency band alone persists in very dilute solutions. The broader, lower frequency band, on the contrary, is the only band of the pair which remains in the spectrum of pure pyrrole. These results, which have also been obtained by Mirone^{2,3} and Tuomikoski,⁴⁻⁶ have been confirmed by Raman spectroscopy.⁷

A number of different hypotheses have been proposed to account for this association. Josien *et al.*,^{1,8,9} and Mirone^{2,3} independently attributed the higher frequency band to the NH vibration of "free" molecules, and the lower frequency band to NH vibrations of pyrrole molecules associated by means of hydrogen bonds of N-H...N type. Tuomikoski^{4,6} questioned the presence of NH...N hydrogen bonding, stating that the graph points for pyrrole "fall into the class of nonhydrogen-bonded liquids"⁶ in both Pauling's¹⁰ and Kumler's¹¹ studies of dipole moment as a

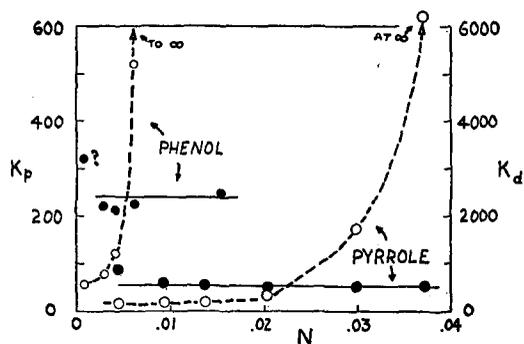


FIG. 1. Dependence of dimer (K_d) and polymer (K_p) equilibrium constants of phenol and pyrrole upon concentration N (molar fraction). The graph is based on data given in reference 16. The K_d (dimer) points are open circles connected by dashed lines; the K_p (polymer) points are black dots connected by solid lines.

function of dielectric constant. Tuomikoski suggested instead the formation of "a dimeric head-to-head association."¹⁶ After the existence of complexes between pyrrole and aromatic compounds was reported,⁸ Tuomikoski proposed another explanation for the pyrrole-pyrrole association, namely, that the NH group of one molecule is associated with the aromatic ring of another pyrrole molecule.^{6,12} Still more recently, having found that the dipole moment of pyrrole is an increasing function of temperature he suggested that pyrrole association is caused by antiparallel dipole orientation.¹³

As a result of this controversy it appeared of interest to us to study molecular association in pyrrole solutions by means of another technique, that of cryoscopy. Prigogine¹⁴ has shown that measurements of the lowering of the freezing point temperature of a solution as a function of solute concentration enables one to distinguish between compounds which form dimeric complexes, for which the equilibrium constant is K_d , and those which form polymeric complexes for which K_p represents an average equilibrium constant.¹⁵

Using Prigogine's cryoscopic technique, we have found¹⁶ that nonpolar cyclohexane solutions of naphthalene, mesitylene, or phenanthrene show, as one would have predicted, practically no association for molar fractions, N , less than 0.02. We also found¹⁶ the cryoscopic behavior of pyrrole and phenol to be similar, since for both compounds K_d varies and K_p is constant, as shown in Fig. 1. Thus the association of pyrrole, like phenol, does not stop at the dimer stage, but continues into polymeric complexes.

Recently an unsuccessful attempt¹⁷ was made to compute a stable value for *some* equilibrium constant of pyrrole using our infrared intensity data¹ for pyrrole in carbontetrachloride solution. We are now repeating these infrared measurements of pyrrole NH band intensities with much higher precision and have preliminary results from which a constant value of K_p for pyrrole has been computed.¹⁸

We feel that the mechanism of hydrogen bonding offers the most satisfactory explanation of pyrrole complexes. Assuming this mechanism, and employing Mirone's suggested zig-zag polymer form^{3,16} enables one to account not only for the direction of the variation of the pyrrole dielectric constant with temperature, but also for the position of the pyrrole dielectric graph points on the Pauling and Kumler graphs.¹⁸

* The part of this work done at Fisk University has been supported jointly by research grant No. C-1520 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service, and by a Frederick Gardner Cottrell Grant from the Research Corporation.

¹ Fuson, Josien, Powell, and Utterback, *J. Chem. Phys.* **20**, 145 (1952).

² P. Mirone, *Atti accad. naz. Lincei, Rend. Classe sci. fis. mat. e nat.* **11**, 365 (1951).

³ P. Mirone and M. Vampiri, *Atti accad. naz. Lincei, Rend. Classe sci. fis. mat. e nat.* **12**, 405 (1952).

⁴ P. Tuomikoski, *J. Chem. Phys.* **20**, 1054 (1952).

⁵ P. Tuomikoski, *J. phys. radium* **15**, 318 (1954).

⁶ P. Tuomikoski, *J. Chem. Phys.* **22**, 2096 (1954).

⁷ P. Chiorboli and P. Manaresi, *Gazz. chim. ital.* **84**, 269 (1954).

⁸ M. L. Josien and N. Fuson, *J. Chem. Phys.* **22**, 1169 (1954).

⁹ M. L. Josien and N. Fuson, *J. Chem. Phys.* **22**, 1264 (1954).

¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948), second edition, p. 293.

¹¹ W. D. Kumler, *J. Am. Chem. Soc.* **57**, 600 (1935).

¹² P. Tuomikoski, *Mikrochim. Acta* **505** (1955).

¹³ P. Tuomikoski, *J. phys. radium* **16**, 347 (1955).

¹⁴ I. Prigogine and R. DeFay, *Thermodynamique Chimique* (Editions Desoer, Brussels, 1950), second edition, p. 434.

¹⁵ Prigogine has shown, for example, that for solutions of benzyl alcohol in nitrobenzene, K_p is constant while K_d varies systematically with concentration, whereas for solutions of phenylacetic acid in the same solvent, it is K_d which remains constant while K_p varies.¹⁴ These results accord with the well-known fact that alcohols form polymers while carboxylic acids form dimers.

¹⁶ Josien, Paty, and Pineau, *Compt. rend.* **241**, 199 (1955).

¹⁷ S. N. Vinogradov and R. H. Linnell, *J. Chem. Phys.* **23**, 93 (1955).

¹⁸ These results will be published elsewhere shortly.

Effect of sp^2 Hybridization of Lone Pair Electrons on the Bond Angle of Nitrogen

H. F. HAMEKA, *Department of Theoretical Organic Chemistry, University of Leiden, Leiden, Netherlands*

AND

A. M. LIQUORI,* *Laboratory of Physical and Inorganic Chemistry, University of Leiden, Leiden, Netherlands*

(Received March 5, 1956)

ACCURATE x-ray studies on a number of azines¹⁻⁴ have shown that there exists a planar structure with bond lengths consistent with MO calculations where complete conjugation is assumed.^{3,5} The values reported for the bond angles show small, but systematic, deviations from 120°. In all cases the bond angle of nitrogen is smaller and that of carbon larger than this value.

An attempt has been made to explain this deviation of the bond angles from the normal value of 120° assuming that sp^2 hybridization of four of the five outer electrons of a nitrogen atom "prepared for bonding" takes place in these molecules. The deformations may then be evaluated by minimizing the energy of an azine with respect to the bond angles.

According to a crude, but often successful model of the chemical bond, the total energy of the valence electrons consists of three parts: (1) the energy necessary to bring the atoms to their valence states, which depends on the promotion energy; i.e., the energy required to promote an electron from a $2s$ to a $2p$ state; (2) the energy of the bonds; and (3) the repulsion energy between electrons in different bonds and lone pairs.

To obtain some idea of the position of the minimum of the energy with respect to the bond angle, a s -triazine molecule was considered first where each nitrogen atom has been depleted of one lone pair electron. (In this case the promotion energy does not depend on the bond angles.) The energy of a chemical bond has been correlated to the overlap integral of the corresponding hybrid orbitals by Mulliken.⁶ After a calculation of these overlap integrals as a function of the bond angles, Mulliken's formula has been used to derive the dependence of the bond energies on the valence angles. For a calculation of the electronic repulsions some simplifications have been made. Only intra-atomic interactions have been considered. Furthermore it has been assumed that the charge distribution of a doubly occupied bonding orbital may be replaced by that of two singly occupied hybrid orbitals from which the bonding orbital has been constructed. With these simplifications the energy could be expressed in one-center Coulomb interaction integrals and the calculation easily made. It appeared that the total energy as a function of the C-N-C angle has a parabolic form with its minimum near 120° as might be expected from symmetry considerations.

The energy of s -triazine could now be obtained by adding the energy, resulting from placing one lone pair electron on each nitrogen atom, to the energy mentioned above. It was then found that the promotion energy, as also the interaction of these lone pair electrons with the other valence electrons on the same atom, were lowered with decreasing C-N-C angle. Consequently the addition of these lone pair electrons caused the C-N-C angles