

dimer. It may be mentioned that a comparable effect of calcium was not observed with quinone, duroquinone, or 1,4- or 1,2-naphthoquinone.

The fact that organic solvents prevent the dimerization, at least in the absence of calcium, is not easy to explain. This effect is quite analogous to the effect of organic solvents on the dimerization of regular (quinonoid, not semiquinone) dyestuffs, such as methylene blue, recognizable by spectrophotometric methods. Here also alcohol prevents dimerization. In alcohol such dyestuffs obey Beer's law: in water they do not because there is an equilibrium established between the monomer and the dimer, depending on concentration and temperature. Furthermore, it may

be added that according to preliminary experiments the dimerization of the free radicals of the "Wurster's dye" type, obtained by partial oxidation of aromatic *para*-diamines, is counteracted also by alcohol to a certain extent.

Summary

The semiquinone radical of phenanthrene-quinone-3-sulfonate is paramagnetic. In aqueous solution it is in equilibrium with its quinhydrone-like, diamagnetic dimer. The dimerization is prevented by pyridine or alcohol. In presence of calcium ion the radical forms a diamagnetic calcium complex of green color.

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[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY, STAMFORD RESEARCH LABORATORIES]

The Dipole Moments of Diazines

BY WILLIAM C. SCHNEIDER

During the course of an investigation of the dipole moments of some thiouracil derivatives,¹ it was deemed desirable to determine the dipole moments of some simpler pyrimidine derivatives and other similar heterocyclic nitrogen compounds in order to obtain a value for the carbon-nitrogen bond moment in this type of molecule which could be used in calculating the electric moments of the more complex thiouracils. Although these thiouracil derivatives later proved to be too complicated for a detailed analysis, the simpler heterocyclic compounds were found to be of sufficient interest in themselves to warrant discussion.

Experimental

The apparatus and measuring technique will be described in another article.¹ Dioxane used as solvent was purified as follows: Commercial dioxane was partially frozen, and the liquid portion discarded. The remaining solid after remelting was refluxed over sodium to remove water and finally distilled through an efficient fractionating column to remove any remaining impurities. The best dioxane obtained in this manner had the

following properties: b. p. (uncor.), 100.5°, d^{25}_4 1.01690, ϵ_{35} 2.1874, n^{25}_D 1.4150.

The compounds investigated are listed in Table I. Table II gives the experimental values of ϵ , dielectric constant, d density and w , weight fraction for dioxane solutions at 35°. Dipole moments were calculated by a modified Hederstrand method similar to that introduced by Halverstadt and Kumler,² differing in that densities were used rather than specific volumes. The empirical equation used may be written as

$$\infty p_T = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \times \frac{1}{d_0} \left[1 - \beta/d_0 \right] + \frac{3\alpha}{(\epsilon_0 + 2)^2 d_0} \quad (3)$$

where ϵ_0 = extrapolated dielectric constant of solvent
 d_0 = extrapolated density of solvent
 ∞p_T = specific polarization at infinite dilution
 α = slope of dielectric constant vs. weight fraction curve
 β = slope of density vs. weight fraction curve.

The total molar polarization at infinite dilution, ∞P_T , is obtained from the specific polarization by multiplying by the molecular weight. Atomic polarization was neglected, and molecular refractions were calculated from the atomic refractions listed in the "Landolt-Börnstein Tabellen." The values obtained from these calculations are listed in Table III, where P_D and P_0 refer to the distortion and orientation polarizations, respectively.

Discussion

To determine whether or not the carbon-nitrogen linkage can be adequately represented by a single constant in heterocyclic ring systems, its moment was calculated from the observed moment of pyridine, $2.3D$,³ assuming a value of $0.4D$ for the carbon-hydrogen link and a plane hexagonal structure for the pyridine ring. A value of $1.9D$

| Compound | M. p., °C. |
|--|------------|
| Pyridazine ^a | |
| Pyrimidine ^a | 18-20 |
| Pyrazine ^b | 52-53 |
| 4-Oxypyrimidine ^b | 163-164 |
| 2,5-Dichloropyrimidine ^c | 57-57.5 |
| 2-Mercapto-5-chloropyrimidine ^c | 221-222 |
| 2-Methoxy-5-chloropyrimidine ^c | 53-54 |

^a Furnished by Dr. R. C. Lord, The Johns Hopkins University. ^b Furnished by Dr. I. F. Halverstadt, these Laboratories. ^c Furnished by Dr. J. P. English, these Laboratories.

(1) Paper to be published shortly.

(2) Halverstadt and Kumler, *THIS JOURNAL*, **64**, 2088 (1942).

(3) Goethals, *Rec. trav. chim.*, **54**, 299 (1935).

TABLE II

| <i>w</i> | ϵ | <i>d</i> | <i>w</i> | ϵ | <i>d</i> |
|----------|-----------------------|-----------|----------|-------------------------------|-----------|
| | Pyridazine | | | Pyrimidine | |
| 0.0 | (2.2090) ^a | (1.01491) | 0.0 | 2.2134 | (1.01689) |
| .0009217 | 2.2348 | 1.01496 | .0001612 | 2.2149 | 1.01691 |
| .001915 | 2.2499 | | .0003038 | 2.2164 | 1.10694 |
| .002854 | 2.2819 | 1.01506 | .0006735 | 2.2195 | 1.01699 |
| .003656 | 2.2908 | | | | |
| | Pyrazine (benzene) | | | 2,5-Dichloropyrimidine | |
| 0.0 | 2.2525 | (0.86283) | 0.0 | 2.2016 | (1.01612) |
| .0007764 | 2.2529 | .86304 | .001232 | 2.2059 | 1.01649 |
| .001540 | 2.2533 | .86320 | .002387 | 2.2134 | 1.01691 |
| .001945 | 2.2528 | .86335 | .003834 | 2.2190 | 1.01728 |
| .002823 | 2.2526 | .86365 | .005288 | 2.2248 | 1.01773 |
| | Pyrazine (dioxane) | | | 2-Mercapto-5-chloropyrimidine | |
| 0.0 | (2.1989) | 1.01623 | 0.0 | (2.2046) | |
| .0005494 | 2.1993 | 1.01630 | .0001938 | 2.2047 | |
| .0009504 | 2.1998 | 1.01638 | .0003652 | 2.2051 | |
| .001548 | 2.2005 | 1.01640 | .0005124 | 2.2043 | |
| .002069 | 2.2009 | 1.01646 | .0006109 | 2.2040 | |
| | 4-Oxypyrimidine | | | 2-Methoxy-5-chloropyrimidine | |
| 0.0 | 2.2057 | 1.01530 | 0.0 | (2.2040) | |
| .0004479 | | | .0004794 | 2.2045 | |
| .0005520 | 2.2119 | 1.01547 | .0007872 | 2.2036 | |
| .001062 | 2.2152 | 1.01568 | .0009427 | 2.2043 | |
| .001294 | 2.2179 | 1.01566 | | | |

^a Values in parentheses obtained by extrapolation.

TABLE III

| Compound | α | β | ∞p_T | Mol. wt. | ∞p_T | P_D | P_e | $\mu \times 10^{18}$ |
|-------------------------------|----------|---------|--------------|----------|--------------|-------|--------|----------------------|
| Pyridazine | 23.523 | 0.1149 | 4.1712 | 80 | 333.7 | 22.1 | 311.6 | 3.94 |
| Pyrimidine | 9.057 | .1485 | 1.7469 | 80 | 139.8 | 22.3 | 117.5 | 2.42 |
| Pyrazine (benzene) | 0.0 | .2650 | 0.2366 | 80 | 18.9 | 22.3 | (-3.4) | (0) |
| Pyrazine (dioxane) | .9666 | .1112 | .4120 | 80 | 32.96 | 22.3 | 10.7 | 0.66 |
| 4-Oxypyrimidine | 9.505 | .2937 | 1.788 | 95 | 169.9 | 23.5 | 146.4 | 2.70 |
| 2,5-Dichloropyrimidine | 4.4062 | .3082 | 0.9330 | 149 | 138.9 | 35.7 | 103.2 | 2.27 |
| 2-Mercapto-5-chloropyrimidine | 0.0 | | | | | .. | | (0.0) |
| 2-Methoxy-5-chloropyrimidine | .0 | | | | | .. | | (0.0) |

was obtained. Using this value, the dipole moments of pyridazine, pyrimidine and pyrazine were calculated, assuming again a plane hexagonal structure for the heterocyclic ring. Table IV lists these calculated values together with experimental values.

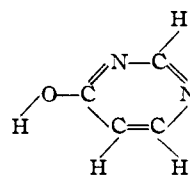
TABLE IV

| Compound | $\mu_{\text{obs.}} \times 10^{18}$ | $\mu_{\text{calcd.}} \times 10^{18}$ |
|----------------------|------------------------------------|--------------------------------------|
| Pyridine (benzene) | 2.3 | ... |
| Pyridazine (dioxane) | 3.9 | 4.0 |
| Pyrimidine (dioxane) | 2.4 | 2.3 |
| Pyrazine (dioxane) | 0.6 | 0.0 |
| (benzene) | .0 | .0 |
| Quinoline (benzene) | 2.2 | 2.3 |

These data allow three important conclusions to be drawn: (1) the carbon-nitrogen electric moment apparently has a constant value in these heterocyclic compounds; (2) a heterocyclic ring of the pyridine type can be represented by a plane, regular hexagon; and (3) in the compounds in-

vestigated, all bonds between nitrogen and carbon seem to be electrically⁴ equivalent.

To obtain an additional check upon the carbon-nitrogen bond moment obtained above, the dipole moment of 4-oxypyrimidine was calculated and compared with the experimental value. This compound may be represented as



where the hydrogen-oxygen linkage exhibits free rotation about the carbon-oxygen axis. Since the resultant moment of the ring acts at an angle to the direction of the carbon-oxygen moment, it is necessary to take into consideration the free ro-

(1) So far as dipolar characteristics are concerned.

tation of the hydrogen-oxygen linkage when calculating a moment for the molecule.

At any given instant the vector diagram for the resultant moment, μ , of the molecule may be represented by Fig. 1. Fuchs⁵ has developed an expression for calculating the average value, $\bar{\mu}$, of the resultant moment which in the present case may be written as

$$\bar{\mu}^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \varphi \cos \theta \quad (2)$$

Using equation (2) and the following assumptions: (1) $\mu_{\text{H-O}} = 1.7D$, (2) $\mu_{\text{C-O}} = 0.7D$, (3) $\mu_{\text{C-N}} = 1.9D$ and (4) an oxygen valency angle of 110° , the dipole moment of 4-oxypyrimidine is calculated to be $2.6D$, which gives satisfactory agreement with the experimental value, $2.7D$.

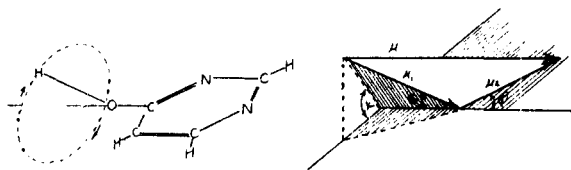


Fig. 1.—Vector representation of the resultant moment of a molecule which has a freely rotating group.

Several additional pyrimidine derivatives were investigated, yielding rather interesting results. Table V lists these compounds and their moments,

| Compound | $\mu \times 10^{18}$ |
|-------------------------------|----------------------|
| 2,5-Dichloropyrimidine | 2.27 |
| 2-Mercapto-5-chloropyrimidine | (0.0) |
| 2-Methoxy-5-chloropyrimidine | (.0) |
| <i>p</i> -Dichlorobenzene | 0.0 ^a |
| <i>p</i> -Chlorophenol | 2.22 ^a |
| <i>p</i> -Chloroanisole | 2.24 ^a |

^a Values taken from *Annual Tables of Constants and Numerical Data*, "Dielectric Constants and Dipole Moments," Vol. 11 Sect. 22 (1931-1934), Hermann and Co., Paris, 1937.

together with the corresponding benzene derivatives. Presumably, the moment of 2,5-dichloropyrimidine is identical with the moment of the pyrimidine ring. The observed moment of pyrimidine, $2.4D$, supports this assumption. Since the moment of 2-methoxy-5-chloropyrimidine can be considered as the resultant of the ring moment and the moment of *p*-chloroanisole, and since these last two moments are essentially identical, the observed zero moment forces one to the conclusion that the resultant of the carbon-chlorine and methyl-oxygen moment exactly opposes the moment of the ring. A similar argument can be used to account for the moment of 2-mercapto-5-chloropyrimidine.

Unless resonance effects in all of the above compounds are identical or the agreement merely fortuitous, the two opposing moments must lie on the same straight line since neither pyrimidine derivative possesses a center of symmetry. The vector

(5) Fuchs, *Z. physik. Chem.*, **14B**, 339 (1931).

representation for the resultant moment of the carbon-chlorine and hydrogen-sulfur-carbon groups is given in Fig. 2. Initially, the hydrogen-sulfur bond is assumed to be in the plane of the paper; the dotted vectors indicate the situation after rotation through 180° . Since the resultant moment always intersects the axis of rotation at the constant angle φ regardless of the position of the freely rotating hydrogen-sulfur vector, it cannot exactly cancel the ring moment unless the valency angle is 180° for then φ will be zero.

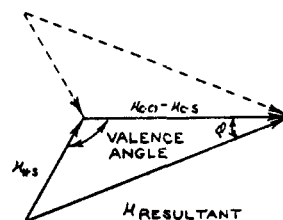
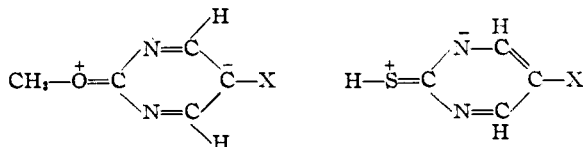


Fig. 2.—Vector representation of the resultant moment of a freely rotating group.

However, in any real molecule the distortion of the valency angle is probably much less than that predicted above for exact cancellation. In para substituted anisoles Bergmann and collaborators in Germany⁶ and Hampson and Sutton in England⁷ concluded that the oxygen valency angle is greater than 110° , the latter authors reporting a value of $142 \pm 8^\circ$.⁸ Opposing this point of view Bennett⁹ concludes that induced moments in the molecule could introduce errors in the method used by the above investigators, and that it is more logical to assume a constant valency angle of 110° and calculate induced moments rather than assume constant bond moments and calculate deviations in the valency angle.

The data are perhaps best interpreted by assuming that an unknown but significant distortion in the valency angle combined with resonance effects causes the hydrogen-oxygen, hydrogen-sulfur or methyl-oxygen link moments to contribute as though they were acting at 180° to the para substituted ring moment. Resonance effects would tend to spread the valency angle slightly and reduce the link moment between the aromatic carbon and oxygen or sulfur atoms due to resonance structures of the type



Using this assumption satisfactory agreement can be obtained between calculated and observed

(6) Bergmann, Engel and Sander, *ibid.*, **10B**, 397 (1930).

(7) Hampson and Sutton, *Proc. Roy. Soc. (London)*, **140A**, 552 (1933).

(8) Hampson, Farmer and Sutton, *ibid.*, **143A**, 147 (1933).

(9) Bennett, *Trans. Faraday Soc.*, 853-858 (1934).

moments for all of the above mentioned compounds and for most of the para substituted anisoles whose moment values are in the literature. Table VI lists observed and calculated moments for several compounds of the type discussed above; Table VII gives the values used for the various bond moments.

The dipole moment of 4-methoxypyridine gives further evidence in support of an abnormal valency angle of oxygen in para substituted derivatives and a constant value of the carbon-nitrogen linkage. Curran and Leis¹⁰ found this compound to have a moment of 2.94*D* in benzene solution. The calculated value obtained using the above assumptions is 3.0*D*.

It must be emphasized that the speculations concerning the valency angle of oxygen and the carbon-oxygen link moment are valid only in the case of *para* substituted derivatives. This fact is immediately obvious if one considers anisole where the observed moment is identical for all practical purposes with that of diethyl ether, thereby requiring a normal carbon-oxygen link moment and

oxygen valency angle of 110°, and a carbon-oxygen link moment of 0.7*D* and the link moments listed in Table VII. Here again, the agreement is satisfactory considering that the observed values were obtained from solution measurements by different workers.

TABLE VII

| | | |
|--------------------|-----------------------|--------------------|
| $\mu_{C-N} = 1.9D$ | $\mu_{C-Cl} = 1.2D$ | $\mu_{C-F} = 1.0D$ |
| $\mu_{H-C} = 0.4D$ | $\mu_{C-NO_2} = 3.5D$ | $\mu_{C-I} = 0.9D$ |
| $\mu_{H-O} = 1.7D$ | $\mu_{C-Br} = 1.1D$ | $\mu_{H-S} = 1.3D$ |

TABLE VIII

| Compound | $\mu_{obs.} \times 10^{18}$ | $\mu_{calcd.} \times 10^{18}$ |
|------------------------|-----------------------------|-------------------------------|
| <i>m</i> -Chlorophenol | 2.14 ^a | 2.1 |
| <i>m</i> -Nitrophenol | 3.90 | 4.0 |
| <i>m</i> -Nitroanisole | 3.86 | 3.7 |

^a See footnote Table VI.

Acknowledgment.—The author wishes to express here his indebtedness to Doctors I. F. Halverstadt and P. H. Bell for many helpful discussions and to the American Cyanamid Company for permission to publish these results.

Summary

1. The dipole moments in dioxane solution at 35° have been determined for the following compounds: pyridazine (3.94), pyrimidine (2.42), pyrazine (0.6), 2,5-dichloropyrimidine (2.27), 2-mercapto-5-chloropyrimidine (0), 2-methoxy-5-chloropyrimidine (0) and 4-oxypyrimidine (2.70).

2. The diazine rings may be represented as plane, regular hexagons.

3. In pyridine and the diazines the carbon-nitrogen linkage has a bond moment of 1.9*D* compared to 0.5*D* in aliphatic compounds.

4. The observed fact that 2-methoxy-5-chloropyrimidine and 2-mercapto-5-chloropyrimidine have zero electric moments is best interpreted by assuming that an unknown distortion in the valence angle combined with resonance effects reduces the link moment between the aromatic carbon and oxygen or sulfur atoms and causes the CH₃-O and H-S link moments to contribute as though they were acting at an angle of 180° to the para substituted ring moment.

5. An analogous situation is assumed to exist in several para substituted phenols and anisoles.

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TABLE VI

| Compound | $\mu_{obs.} \times 10^{18}$ | $\mu_{calcd.} \times 10^{18}$ |
|-------------------------------|-----------------------------|-------------------------------|
| 2,5-Dichloropyrimidine | 2.27 | 2.3 |
| 2-Mercapto-5-chloropyrimidine | 0 | 0 |
| 2-Methoxy-5-chloropyrimidine | 0 | 0 |
| <i>p</i> -Chloroanisole | 2.24 ^a | 2.3 |
| <i>p</i> -Bromoanisole | 2.25 | 2.2 |
| <i>p</i> -Iodoanisole | 2.12 | 2.0 |
| <i>p</i> -Fluoroanisole | 2.09 | 2.1 |
| <i>p</i> -Nitroanisole | 4.76 | 4.6 |
| <i>p</i> -Chlorophenol | 2.40 | 2.9 |
| <i>p</i> -Bromophenol | 2.6 | 2.8 |
| <i>p</i> -Nitrophenol | 5.03 | 5.2 |
| <i>p</i> -Nitrodiphenyl ether | 4.3 | 4.6 |
| <i>p</i> -Nitrosophenol | 4.72 | 4.5 |

^a All observed values not obtained in this investigation were taken from the Appendix in the *Trans. Faraday Soc.*, "Discussion of Dipole Moments" (1934).

an oxygen valency angle of 110°. This viewpoint is further substantiated if one considers the meta substituted isomers. Table VIII compares observed and calculated values for various meta substituted derivatives. The calculated values were obtained by use of equation (2) assuming an

(10) Curran and Leis, *THIS JOURNAL*, **67**, 79-81 (1945).