CHARGE DISTRIBUTION AND DIPOLE MOMENT OF PYRIDINE*

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The π-electron distribution in pyridine has been calculated recently using the SCFMO method (Brown and Heffernan 1957a). The charge distribution may also be calculated by a configuration interaction treatment as has been done for the simple two-centre systems $CH_2=NH_2^+$, $CH_2=NH$, $CH_2=N^-$ (Brown and Penfold 1956, 1957) and $CH_2=O$ (Brown and Heffernan 1957b). We have used the Parr-Pariser (1953) treatment, including limited configuration interaction. The ground state charge distribution is obtained by mixing together the charge distributions of all the singlet configurations that have the ground state symmetry, namely $^1A_1$. In the present calculations we have included only those configurations which arise from the excitation of an electron from the two highest bonding orbitals in pyridine up to the lowest two antibonding π-orbitals (in the case of benzene these correspond to doubly degenerate bonding and antibonding orbitals respectively). We thus obtain two singlet configurations

Φ_1 and Φ_2, which mix with the ground state configuration Φ_0, to give the final ground state wave-function :

$$\Psi_0 = A_0\Phi_0 + A_1\Phi_1 + A_2\Phi_2.$$

The coefficients A_0, A_1, and A_2 were obtained by solution of the appropriate secular equations using the values of the matrix elements derived in a treatment of the ultraviolet spectrum of pyridine (Brown, Heffernan, and Penfold, unpublished data). The charge distribution in the ground state was obtained from these coefficients using formulae analogous to that given by Taylor (1951), but simplified by the assumption of zero differential overlap (Pariser and Parr 1953). The π-electron densities $P_{\mu\mu}$ obtained in this way are compared with those previously found by the SCF method in Table 1.

As in the case of previous calculations (Brown and Heffernan 1957a, 1957b ; Brown and Penfold 1956, 1957) the configuration-interaction (ASMOCI) charge densities correspond to an overall smaller charge separation than do the SCF values. The disparity between the two sets of results is about the same as in former calculations, indicating that the configurations of $^1A_1$ symmetry with higher energies than those included in the present calculations probably do not influence the charge distribution appreciably.

TABLE 1

CHARGE DISTRIBUTION IN PYRIDINE

Method	P_{NN}	$P_{\alpha\alpha}$	$P_{\beta\beta}$	$P_{\gamma\gamma}$
SCFMO ..	1·061	0·999	0·983	0·974
ASMOCI ..	1·027	1·013	0·987	0·973
SCE*	1·031	1·000	0·991	0·987

* These values were obtained from the SCFMO values by halving the formal charges found by the SCF method.

The third charge distribution listed in Table 1 is an estimate of the result which would be obtained by the self-consistent electronegativity (SCE) method (Brown and Heffernan 1957a). The full SCE calculations have not so far been performed for pyridine but the present values have been estimated using the observation that charge separations found by the SCE method are very close to half those found by the SCFMO method.

The present results may be used to evaluate the π-electron contribution to the molecular dipole moment. In the case of formaldehyde (Brown and Heffernan 1957b) the dipole moment could be accounted for entirely in terms of hybridization moments plus a small π-electron moment, the latter being derived from SCE charge distribution. The same analysis may now be applied to the pyridine system. We have used the SCE charge distribution and the geometry previously quoted (Brown and Heffernan 1957a). The valence electrons are symmetrically disposed around each carbon atom so that no contribution is made to the molecular dipole. The moments arising from

hybridized valence orbitals for the hydrogen atoms cancel one another in the case of the β- and α-hydrogens, but the valence orbital of the γ-hydrogen atom results in a hybridization moment with the negative end directed towards the nitrogen atom. This reinforces the hybridization moment arising from the nitrogen valence electrons owing to the uncompensated electron in the sp^2 lone-pair orbital. When the small π-electron moment is added to these hybridization moments the total comes to 2·33 D (Table 2), which is in surprising agreement with the experimental value of 2·25 D (Wesson 1948). This strongly suggests that there is no appreciable polarization of the C—N σ-bonds, that is, that these bonds are purely covalent.

TABLE 2

THE DIPOLE MOMENT OF PYRIDINE

Contribution	Value (D)
π-electron moment..	0·356
H-hybridization	0·199
N-hybridization	1·778
Total	2·333

The fact that the σ-electron polarization is negligible may alternatively be deduced from the very small polarization of π-electrons found in the present calculations. Since σ-electrons are less easily polarized than π-electrons, the σ-electron polarization must be expected to be even smaller and so for most purposes negligible. A similar conclusion has been reached for the C—O σ-electrons in formaldehyde, and the same probably applies therefore to conjugated heterocyclic systems generally.

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THE USE OF POTASSIUM CHLORIDE DISKS IN THE INFRA–RED EXAMINATION OF FIBROUS CELLULOSE AND OTHER SOLID MATERIALS*

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Potassium bromide was used in the early work on the pressed alkali halide disk method for the infra-red examination of solid samples by Schiedt and Reinwein (1952), Stimson and O'Donnell (1952), Anderson and Woodall (1953), and Hausdorff (1953). For this reason, probably, potassium bromide continues to be used in preference to potassium chloride, which has several advantages, as pointed out by Hales and Kynaston (1954). Potassium chloride has a lower chemical reactivity and a greater stability to heat than potassium bromide, and the slightly higher pressure required for flow is immaterial in practice. It is less hygroscopic and easier to grind to a satisfactory particle size without taking up moisture. Ford and Wilkinson (1954) recognized that potassium chloride was as suitable as potassium bromide, and that sodium chloride, while otherwise satisfactory, required a much higher pressure owing to its greater lattice energy.

Having examined the relative merits of these three halides, we would support the use of potassium chloride. Stable disks and well-defined spectra of a range of solid materials, mostly of high molecular weight, have been obtained without the use of a dry box. With potassium chloride disks, the absorption over most of the rock-salt region of the spectrum does not exceed 2 or 3 per cent., and with appropriate care only very small absorption bands at $2 \cdot 9$ and $6 \cdot 1$ μ remain, owing to the water present. With potassium bromide, changes have been observed in spectra with time (Barker *et al.* 1956) and difficulties have been encountered in the study of simple mixtures (Bak and Christensen 1956); it is not known whether these disadvantages apply also to potassium chloride disks. Farmer (1955) has suggested that misleading results may sometimes be obtained by the disk technique when it is applied to compounds containing hydroxyl groups. However, it would be unfortunate if the considerable advantages of the alkali halide disk method over the use of mulls were to be underestimated on account of relatively minor difficulties. The absorption bands of the paraffin tend to mask those of the specimen, mulling does not lend itself readily to quantitative treatment or to keeping the dispersed sample for further examination, the Christensen effect is likely to be more pronounced with mull spectra (Ford and Wilkinson 1954) and very small samples cannot be dealt with as readily as by the disk technique.

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