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THE SCMO CHARGE DENSITIES OF THE PURINE MOLECULE[a]

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IN a recent criticism[1] of a Hückel calculation on purine[2] the comment was correctly made that this method yields an erroneous reactivity order when referred to the pi-electronic charge distribution in that molecule.[3] One may also add that a similar, i.e. Hückel, localization energy calculation will not put the matter entirely right,[4] nor will appeal to frontier electron densities yield a result consistent with experimental findings.[4] In a similar way, the Hückel charge desnities do not predict correct basisities for the several nitrogen atoms in this system.

On the basis of our calculations we feel that this is because the simple LCAO method as usually implemented, is not sensitive to the geometry of the molecule, and because the nitrogen atoms of the glyoxaline ring are usually not clearly distinguished. The fundamental assumptions involved are too drastic to correctly assess the required charge distributions.

We have carried out a semi-empirical self consistent molecular

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orbital (SCMO) calculation on the pi-electrons in the purine molecule using the methods developed by Adams and Lykos.[5] The geometry of the system was adapted from that suggested by Cochran[6] in his X-ray determination of adenine, and the parameters used were those of Pariser and Parr[7] and Paoloni and Dewar[8] as revised in the light of Pritchard and Skinner's more recent determinations.[9]

TABLE 1

A Comparison of Hückel and SCMO Charge Densities for the Purine Molecule

Atom	SCMO	Hückel
N1	1.2698	1.266
C2	0.7937	0.844
N3	1.2401	1.283
C6	0.7812	0.864
C8	0.9103	0.820
N6	1.2312	1.488
N7	1.7798	1.493

The SCMO charge distributions are collected and compared to the corresponding Hückel values[10] in Table 1 using the numbering system as indicated in Fig. 1. It is of particular importance to note that we have designated (on the basis of comparative calculations) N7 as contributing two pi-electrons to the delocalized system. This has been taken cognizance of in the evaluation of the one-center core integrals over atomic orbitals within the framework of the Goeppert-Mayer and Sklar[11] expansion of the "core"

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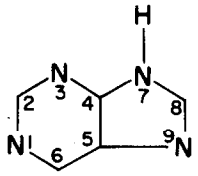

FIG. 1

The numbering system used for the purine molecule.

potential. The results reveal that the SCMO method leads not only to the correct order of electrophillic and/or nucleophillic substitution but also characterizes N1 as the most basic, in accordance with experimental evidence.

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