CNDO/2 Calculations of Some Polyazaindenes

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The theoretically estimated dipole moments of indolizine, imidazo[1,2-a]pyridine, imidazo-[1,5-a]pyridine and of pyrazolo[1,5-a]pyridine obtained by the CNDO/2 approximation have been compared with the experimental values. The bond angles and bond distances for these polyazaindenes have been estimated.

The chemistry of polyazaindenes has recently been the subject of numerous publications from this and other laboratories (1,2,3,4,5). These studies have elaborated the behavior of these compounds to electrophilic agents, alkylation, and *H-D* exchange under basic, as well as acidic conditions. The complex nmr spectra of these substances have been analyzed and the chemical shifts of the various protons have been correlated to some extent with the π-electron densities as estimated by the HMO technique (5).

We now wish to report the results of CNDO/2 calculations on indolizine (1), imidazo[1,2-a]pyridine (2), imidazo[1,5-a]pyridine (3), pyrazolo[1,5-a]pyridine (4) (*cf.* footnote b in Table II) and correlations of these calculations with some experimentally determined properties of these molecules.
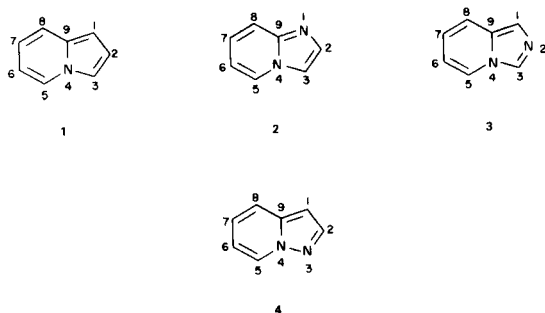
It has been well established that the CNDO/2 method reproduces the geometry of molecules quite well (6,7). Thus, one can calculate the bond lengths and bond angles by a series of calculations aimed at minimizing the total energy of the molecule in question. In the absence of any knowledge of experimentally determined bond distances, this approach is, of course, laborious, if not impossible for larger molecules.

While the geometries of compounds 1 through 4 have not yet been established, the bond lengths and angles of the related s-triazolo[2,3-c]pyrimidine (5) are known (8).
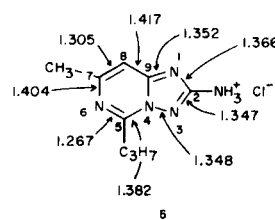
Thus, one can use the s-triazolo[2,3-c]pyrimidine parameters as "starting points" in attempting to estimate the bond lengths and angles of indolizine (1) and its various aza-analogs (2-4).

The approach that we took to obtain these parameters can be exemplified by describing the *modus operandi* employed in calculating the bond lengths and bond angles for pyrazolo[1,5-a]pyridine (4). In this molecule the C_5-C_6, C_1-C_9 and C_2-C_3 bonds will differ significantly from the C_5-N_6, N_1-C_9 and the N_1-C_2 bonds, respectively in compound 5.

By assuming that the C_5-C_6 and C_7-C_8 bonds in compound 4 are the same as the C_7-C_8 bond in compound 5, we are left with having to modify the C_1-C_9 and C_2-C_3 bonds in compound 4. This can be done by successively changing these values until the CNDO/2 calculations show a minimum in the total energy of compound 4. The reality of the values thus obtained can then be checked by using the C_1-C_9 bond length for compounds 1 and 3, respectively, and the C_2-C_3 bond length thus obtained, in the indolizine (1) C_1-C_2 bond situation. All of the other bond lengths and bond angles can be similarly approximated.

The sensitivity of the CNDO/2 method to changes in bond lengths and bond angles is demonstrated by comparing the results obtained from the above considerations with those obtained by assuming that the geometry of imidazo[1,2-a]pyridine approximates that of purine (Table I).

TABLE I

Dipole Moments and Binding Energies For Some Polyazaindenes

	Binding Energy (a)	Theoretical Dipole Moment (Debye)	Experimental Dipole Moment (Debye)
structure	-8.751	1.33 (1.98)(b)	1.13
structure	-8.315	3.22 (4.35)	3.47
structure	-8.300	3.27 (3.67)	3.25
structure	-8.327	2.6 (2.75)	2.18

(a) Values are in Hartrees. (b) Numbers in parentheses refer to the dipole moments as obtained by assuming purine bond lengths and angles.

TABLE II

CNDO/2 Electron Densities of the Various Positions of Indolizine and Some of its Aza-analogs

	1	2	3	4

Carbon and Nitrogen

	1	2	(HMO)	3	4
1	4.080	5.171	(1.462)(a)	4.012	4.067
2	4.018	3.894	(1.036)	5.162	3.939
3	3.967	4.067	(1.112)	3.887	5.166
4	5.015	5.051	(1.482)	5.035	4.894
5	3.899	3.927	(.927)	3.903	3.896
6	4.032	4.006	(1.022)	4.025	4.031
7	3.993	3.974	(.976)	3.984	3.966
8	4.023	4.019	(1.017)	4.019	4.026
9	3.906	3.857	(.954)	3.924	3.896

Hydrogen

	1	2	3	4
1	1.001	-----	.996	-----
2	1.003	1.018	-----	.971
3	1.024	1.007	1.011	1.029
5	1.021	1.011	1.020	1.002
6	.994	.987	.992	1.009
7	1.000	1.007	1.011	.989
8	1.006	0.992	1.004	1.015

(a) Numbers in parentheses refer to HMO calculations. (b) This numbering is used to maintain consistency for comparison purposes with that used for compounds 1 to 3.

A most adequate means of establishing a link between the results of CNDO/2 calculations with a physical property of these compounds is found in a comparison with the experimental dipole moments.

The results of these comparisons (cf. Table I) clearly allow one to place some credence in the CNDO/2 results. We might hope that the bond lengths and bond angles obtained by the CNDO/2 method will be in agreement with experimentally determined values that may become available in the future.

Because of the coincidence of the theoretical and experimental dipoles, we can have some confidence that earlier comments (3), suggesting that these systems are essentially planar, are valid and that the CNDO/2 calculations reproduce the experimental electron densities at the various atoms to a satisfactory extent. As would be expected from resonance considerations, we find that all of the bridge-head nitrogens have a lower electron density associated with them than do the non-bridge-head ones. This difference becomes more pronounced the closer the non-bridge-head nitrogen is to the bridge-head one (the N_4 density in compound 4 is 4.894, while it is somewhat larger than 5.0 in the other compounds).

We also find that compound 4 has a larger binding energy, in agreement with the fact that the molecule has a N-N bond, than do the other two azaindolizines (2 and 3) (cf. Table I).

A comparison of the binding energies of compounds 2 and 3, where one can expect the resonance contributors 2a and 3a to be involved, suggests, as predicted, that the ortho-quinoid contributor 3a does not add to the ground-state stabilization as much as does the pyridinoid contributor 2a .

TABLE III

Optimum Bond Lengths and Bond Angles
for the CNDO/2 Calculations
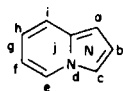
	Bond			
	1	**2**	**3**	**4**
a	1.35	1.35	1.35	1.33
b	1.37	1.40	1.37	1.40
c	1.32	1.33	1.32	1.36
d	1.35	1.35	1.35	1.37
e	1.35	1.35	1.35	1.35
f	1.32	1.32	1.32	1.32
g	1.41	1.41	1.41	1.41
h	1.32	1.32	1.32	1.32
i	1.44	1.44	1.44	1.44
	Angle			
aj	112	113	112	107
ab	106	103	106	116
bc	107	109	107	97
cd	114	114	114	118
dj	101	101	101	102
je	111			
ef	130			
gf	117			
gh	119			
hi	123			
ij	120			
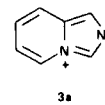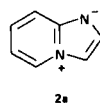
EXPERIMENTAL

The CNDO/2 calculations were done with the G. A. Segal program (No. 91) obtained from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, modified for use on an IBM-360-44 system and including the calculation of binding energies and total dipole moments.

The experimental dipole moments were determined in benzene solution with a Heterodyne-Beat Dipole Moment apparatus described by A. C. Vandenbroucke, Jr., R. W. Kind and J. G. Verkade, The Review of Scientific Instruments, 39, 558 (1968).

The purity of the compounds was established by tlc and, where applicable, by gas chromatography. Their syntheses have been described in references 1, 2, 4 and 5.

The bond lengths and bond angles used for these calculations are listed in Table III.

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