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Lone-Pair Electronic Effects on the Calculated ab Initio SCF-MO Electric Potential and the Crystal Structures of Azabenzenes

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Abstract: Molecular charge distribution models for pyridine, pyridazine, pyrimidine, pyrazine, *s*-triazine, and *s*-tetrazine were evaluated from SCF-MO wave functions. Potential-derived net atomic charges and lone-pair electron site charges were obtained from the calculated electrostatic potential around the molecules. The charge site models were tested by using them to predict the crystal structures of pyrimidine, pyrazine, *s*-tetrazine, and two forms of *s*-triazine by molecular packing analysis.

The continuing interest in understanding intermolecular interactions[1-4] and crystal packing has placed an importance on the concept of net atomic charges. Besides crystal packing energy calculations, net atomic charges are important in understanding the molecular dipole moment and have been used as an index of reactivity of atomic sites in molecules. Problems arise, unfortunately, since the net atomic charge is not an exactly defined physical quantity and approximations must be made in its calculation.

To the first approximation for a neutral molecule, the electrostatic potential is zero at a distance outside the boundary of the electron cloud. However, it has long been known from electronegativity studies that even in neutral molecules the electron clouds does not distribute itself in such a way as to yield a zero electrostatic potential at relatively close distances. It is convenient to regard this electrostatic potential around the molecule as arising from the presence of net atomic charges.

Until recently, the population analysis method of Mulliken[5] has been the most widely used method for the determination of net atomic charges in molecules. The population analysis (PA) net atomic charges are obtained from the coefficients of a molecular orbital wave function which must be formed from a linear combination of atomic orbitals (LCAO-MO method). PA net atomic charges are not a definable quantum mechanical physical property, but they have gained wide use since they show trends which correlate well with electronegativity and chemical reactivity. PA charges are not defined for wave functions which are not of the LCAO-MO type.

A number of attempts have been made to obtain net atomic charges by other methods. The most recent development has utilized the idea of first calculating the electrostatic potential at points in space around the molecule and then finding by a least-squares fitting technique the optimum net atomic charges which will best reproduce the surrounding molecular potential.

In contrast to the population analysis charges, the electrostatic potential around a molecule is a rigorously defined quantum mechanical property. Scrocco and Tomasi[6] in a recent review discussed the calculation of the molecular electrostatic potential from the molecular wave functions and its correlation to molecular reactivity and intermolecular forces. The recent development of ab initio self-consistent field molecular orbital (SCF-MO) calculations and advances in digital computing have made available high quality molecular wave functions for small molecules. The electrostatic potential at points in space around these molecules can be calculated directly from the SCF-MO wave functions. Net atomic charges can be found from these wave functions which best reproduce the calculated SCF-MO electrostatic potential around the molecule by a least-squares fitting process. These net atomic charges are designated potential-derived (PD) to distinguish them from the population analysis (PA) charges.

Momany[7] has determined PD charges in this way for methanol, formamide, and formic acid. Smit, Derissen, and Van Duijneveldt[8] have reported PD charges for methanol, formaldehyde, and formic acid. Cox and Williams[9] reported PD charges for a variety of small molecules. They used three different wave functions. These wave functions were formed from either a minimal basis set,[10] STO-3G, a split valence basis set,[11] 6-31G, or an extended basis set,[11] 6-31G**. The molecules considered were hydrogen fluoride, water, methane, acetylene, ethylene, carbon dioxide, formaldehyde, methanol, formamide, formic acid, acrylonitrile, diborane, and the carbonate ion. In all cases the PD charges gave a more accurate portrayal of the electrostatic potential and the experimentally determined dipole moments than PA charges.

Cox, Hsu, and Williams[12] used the minimal basis set STO-3G to calculate the electrostatic potential and to derive PD net atomic charges for carbon dioxide, trioxane, tetroxocane, pentoxecane, succinic anhydride, 1,4-cyclohexanedione, *p*-benzoquinone, diglycolic anhydride, and furan. These PD charges were subsequently incorporated into (exp-6-1) nonbonded interatomic potential functions which were used to predict the crystal structures.

Recently, Cox[13] has evaluated PD charges for a series of organic cyano-substituted molecules: ethanedinitrile, dicyanoacetylene, tetracyanoacetylene, *cis*-1,2,3-tricyanocyclopropane, 1,1,2,2-tetracyanocyclopropane, and *cis-trans-cis*-1,2,3,4-tetracyanocyclobutane. He found that PD charges could be obtained for these molecules which reproduced the electrostatic potentials, and also the crystal structures, without using lone-pair electron sites on the nitrogen atoms.

In attempting to extend his work to aromatic nitrogen compounds, Cox found that a good fit to the SCF-MO electrostatic potential of *s*-tetrazine, for example, could not be obtained with net atomic charges alone. He found that placement of lone-pair electron sites in the ring plane several tenths of an angstrom out from the nitrogen nucleus greatly improved the fit of the PD model for the electrostatic potential. Coincidentally, it was noticed that only a poor fit could be obtained for the crystal structure of *s*-tetrazine by molecular packing analysis[14] (MPA) if only net

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Table I. Structural Data for Azabenzenes

substance	ref for mol structure	ref for cryst structure	space group	obsd lattice constants a	b	c	β
pyridine	32	47	$Pna2_1$	17.524	8.969	11.352	–
pyridazine	33	–					
pyrimidine	34	34	$Pna2_1$	11.698	9.493	3.806	–
pyrazine	35	36	$Pmnn$	9.316	3.815	5.911	–
α-*s*-triazine	37	38	$R\bar{3}c$	9.647	9.647	7.281	–[a]
β-*s*-triazine	37	29	$C2/c$	6.884	9.569	7.093	126.61
s-tetrazine	39	40	$P2_1/c$	5.23	5.79	6.63	115.50

[a] The trigonal cell is referred to hexagonal axes, $\gamma = 120.00$.

atomic charges (and no lone-pair charges) were used. Since MPA was successful for the above-mentioned cyano compounds, and also for triethylene diamine,[13] we hypothesized that the lone-pair electron effect might be most significant in aromatic nitrogen heterocyclic molecules. The present work was undertaken as a systematic study of lone-pair electron site effects on the PD model for azabenzenes, aiming toward successful application of MPA for prediction of the crystal structures of these molecules. Previous work on the modeling of the crystal structures of azabenzenes has not utilized lone-pair electron sites.

The main objective of MPA is to predict the static equilibrium crystal structure. Usually the space group symmetry is assumed or, if appropriate, energy minimizations can be carried out in several space groups. Also, the molecule is usually assumed to be rigid, a requirement that is well satisfied in the present case. In this work the success of the MPA model is measured against how well it predicts the observed lattice constants, and the molecular translational and rotational orientation in the cell.

Apparently the only model for any of the azabenzenes which has been tested against the static crystal structure is that of Reynolds[15] for pyrazine. Rae[16] performed partial static structure tests for the two crystalline forms of *s*-triazine: the angle of shear of the unit cell was calculated as well as the molecular rotation angle; the cell edge lengths were held fixed. The less stringent test of predicting only the molecular orientation was used for pyrazine by Sandford and Boyd[17] and for several azabenzene molecules by Gamba and Bonadeo.[18,19]

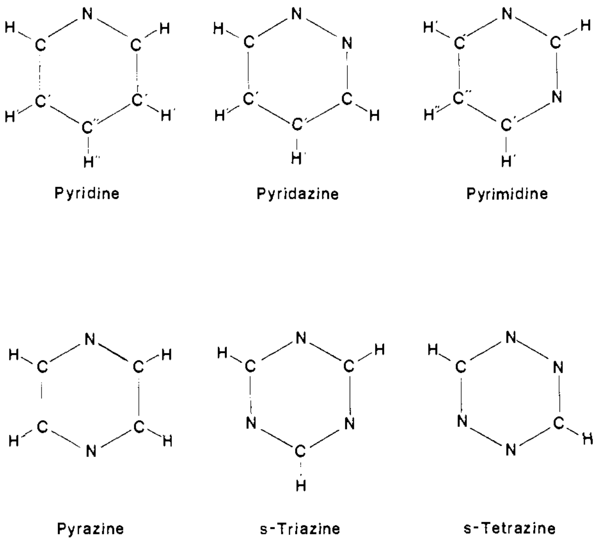
Method

The electrostatic potential at points in space around the molecules was calculated by using the SCF–MO program GAUSSIAN 79.[20] As a compromise[9,21] between the required computer time and the accuracy of the obtained wavefunction, the 6-31G basis set[11] was selected. The electrostatic potential for a unit positive charge at a point **r** in the vicinity of the given molecule containing nuclei with charge Z_A at positions $\mathbf{R}_A$ is given by

$$V(r) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \sum_{mn} P_{mn} \int \frac{\phi_m \phi_n}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'$$

where P_{mn} is an element of the density matrix of the SCF–MO molecular wave function and ϕ_m are the atomic wave functions used as a basis set. The second term is summed over all of the electrons of the system.

The set of points selected for the evaluation of the electrostatic potential was a cubic grid of 1 Å spacing in a 1.2 Å thick shell around the molecule. The inner surface of this shell was selected to represent the distance of closest intermolecular approach and was taken at the van der Waals radius of the nearest atom plus the van der Waals radius of the smallest possible approaching atom, hydrogen. The van der Waals radii of C, N, and H atoms were taken as 1.7, 1.5, and 1.2 Å. This procedure led to the definition of about 300 grid points around each molecule where the electrostatic potential was evaluated from the SCF–MO wave function.


Pyridine Pyridazine Pyrimidine

Pyrazine s-Triazine s-Tetrazine

Figure 1. The molecules considered and their atomic designations.

The PD model assumes that the electrostatic potential around the molecule can be approximated by placing variable point charges at sites within the molecule. If these sites are the atomic nuclei, the model is no-lone pair (NLP). If lone-pair electron sites are also included, the model is lone pair (LP).

The site charges for the NLP and LP models were fitted to the molecular electrostatic potentials at the grid points by a least-squares technique. The criterion of fit was the sum of squares function, which for m grid points and n atoms is given by

$$R = \sum_i^m w_i \{V_i^0 - \sum_j^{n-1} q_j r_{ij}^{-1} + (\sum_j^{n-1} q_j - Z) r_{in}^{-1}\}^2$$

where V_i^0 is the calculated quantum mechanical electrostatic potential at point i, q_j is the site charge at site j, r_{ij} is the distance between site j and the ith grid point, and Z is the net charge on the molecule (zero for the molecules here considered). The number of independent site charges will be decreased by one since there is the dependency condition that the sum of the site charges be equal to Z. Also, the symmetry of the molecule will establish further dependency conditions.

The minimum value of R was found by taking the first partial derivatives of R with respect to the independent charges and solving the resulting set of linear equations by the usual least-squares method. The statical weight, w_i, for each point was taken as unity, which had been found satisfactory by Cox and Williams.[9] In order to make comparisons between various models it was useful to define the root-mean-square fit parameter, σ, as

$$\sigma = \{m^{-1} \sum_i (V_i^0 - V_i^{\text{model}})^2\}^{1/2}$$

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and a relative root-mean-square fit, s, expressed as

$$s = \sigma/\{m^{-1}\sum_i (V_i^0)^2\}^{1/2}$$

Accurate bond distances and angles for most of the azabenzene molecules considered are available from their moments of inertia derived from rotational spectra. Figure 1 shows the atomic designations of the azabenzene molecules which were considered. Table I gives references to the molecular geometry used in each case. For pyrimidine the molecular distances and angles were taken from the crystal structure, since a spectroscopic structural determination was not available for this molecule. The carbon–hydrogen bond distances from X-ray diffraction data were lengthened by 0.07 Å to correct for foreshortening[22] caused by the shift of electron density into the bond and away from the proton position.

The PA, NLP, and LP site-charge models obtained from the SCF–MO calculations were tested by using them to predict the observed crystal structures of these azabenzene molecules, where they are known. The crystal structure of pyridine was not treated because of its complexity; it has four molecules in the crystallographic asymmetric unit. The pyridazine crystal structure was not available. *s*-Triazine has been determined in two crystalline modifications. Table I gives references to the observed crystal structures and gives the observed space groups and lattice constants. In all the MPA calculations foreshortened[22] C–H bond lengths were used.

The crystal lattice energies were minimized by using the computer program PCK6.[14,23] The dispersion and exchange repulsion nonbonded potential parameters for carbon and hydrogen were taken from Williams and Starr.[24] The nonbonded potential parameters for nitrogen were taken from Cox.[13] These values are $A_{CC} = 2414$, $B_{CC} = 367250$, $C_{CC} = 3.60$, $A_{NN} = 1472$, $B_{NN} = 320000$, $C_{NN} = 3.78$, $A_{HH} = 136$, $B_{HH} = 11677$, and $C_{HH} = 3.74$ in units of kJ mol^{-1} and Å. The heteroatomic nonbonded potential parameters were taken as the geometric mean. Note that these nonbonded potential parameters were not adjusted to fit the crystal structures treated.

Three site charge models were considered: net atomic charges obtained by population analysis (PA); PD charges using atomic sites only (NLP); and PD charges using additional lone-pair sites (LP). For the MPA calculations the NLP and LP site charges obtained from the calculated SCF–MO electrostatic potential using the 6-31G basis set were scaled by a factor of 0.82. This scale factor was used because this basis set is known to overestimate the PD charges by approximately this amount.[9] The PA charges were not scaled.

Convergence acceleration[25] was used to increase the accuracy of the evaluation of the crystal lattice sums. The convergence constant was taken as 0.150; at this value the reciprocal lattice contribution to the total was determined to be less than 1% and was neglected. The direct lattice sum was evaluated to a 9 Å limit, always with inclusion of an entire molecule if any atom was within this distance of any atom in the reference molecule. The total error in the evaluation of the lattice sums was estimated as less than 1%; this estimate does not include any errors in the nonbonded parameters or in the site charges.

Starting from the observed structure, the lattice energy was minimized until all structural parameter shifts were less than 0.0005 Å or 0.0005 rad or the energy decrease was less than 0.0002 kJ mol^{-1} per Newton–Raphson cycle.

Results and Discussion

Table II shows the site charges obtained for each atom of each molecule, for the three models: population analysis (PA), potential-derived with no pair sites (NLP), and potential-derived with lone pair sites in the ring plane 0.25 Å out from nitrogen (LP). Figure 2 shows how the goodness of fit index σ and the lone-pair site charge varies with the lone pair distance for each molecule.

Table II. Site Charges for Azabenzenes in Electronic Units × 10^3 [a]

molecule/ dipole moment	quantity	PA	NLP	LP
pyridine	q_N	−527	−934	1607
$u_0 = 2.15^{41}$	q_C	52	768	−146
$u_{SCF} = 2.74$	$q_{C'}$	−238	−821	−216
	$q_{C''}$	−158	497	−70
	q_H	207	−11	166
	$q_{H'}$	214	256	162
	$q_{H''}$	215	53	149
	q_{LP}			−1618
	σ	10.6	1.6	0.7
	s	42.3	4.5	2.0
	u_c	3.11	2.73	2.74
pyridazine	q_N	−288	−421	1242
$u_0 = 4.22^{42}$	q_C	12	596	−143
$u_{SCF} = 5.11$	$q_{C'}$	−188	−311	−147
	q_H	231	−56	177
	$q_{H'}$	231	192	171
	q_{LP}			−1300
	σ	14.0	4.3	0.6
	s	33.8	7.3	1.1
	u_c	5.75	5.03	5.10
pyrimidine	q_N	−502	−1046	1301
$u_0 = 2.334^{43}$	q_C	214	1084	−96
$u_{SCF} = 2.93$	$q_{C'}$	87	894	−31
	$q_{C''}$	−246	−1051	−328
	q_H	227	−41	188
	$q_{H'}$	216	−5	173
	$q_{H''}$	203	322	202
	q_{LP}			−1426
	σ	12.3	1.7	0.5
	s	43.9	4.4	1.3
	u_c	3.08	2.94	2.93
pyrazine	q_N	−476	−580	1628
	q_C	12	236	−213
	q_H	226	54	191
	q_{LP}			−1584
	σ	13.3	3.0	0.6
	s	67.9	10.7	2.2
s-triazine	q_N	−467	−1102	1102
	q_C	218	1115	18
	q_H	249	−13	185
	q_{LP}			−1305
	σ	28.7	1.6	0.6
	s	181.0	7.3	2.5
s-tetrazine	q_N	−230	−491	1223
	q_C	181	1167	−175
	q_H	279	−186	237
	q_{LP}			−1254
	σ	19.2	5.9	0.6
	s	75.9	16.6	1.6

[a] Dipole moments are given in Debye units, σ is given in kJ/mol, and s in percent. The distance from the nitrogen to the lone pair site in the LP model is 0.25 Å.

The figure shows that the best fit to the calculated electric potential was obtained with the lone pair being located from <0.02 Å (pyridine) to 0.23 Å (tetrazine) from the nitrogen atom. The optimum distances (Å) and charges (electrons) are: pyridine, <0.02, <−25.76; pyridazine, 0.03, −12.65; pyrimidine, 0.06, −6.52; pyrazine, 0.06, −7.68; triazine, 0.04, −8.90; tetrazine, 0.23, −1.25.

It could be argued that the lone-pair electronic charge should not be more negative than −2 electrons. Figure 2 shows that most of the benefit of the LP model is retained for all molecules considered for a lone pair distance of up to about 0.25 Å. At this distance all lone-pair site charges are less than 2 in magnitude; they range from −1.62 for pyridine up to −1.25 for *s*-tetrazine. The smaller site charges of the 0.25-Å LP model are desirable

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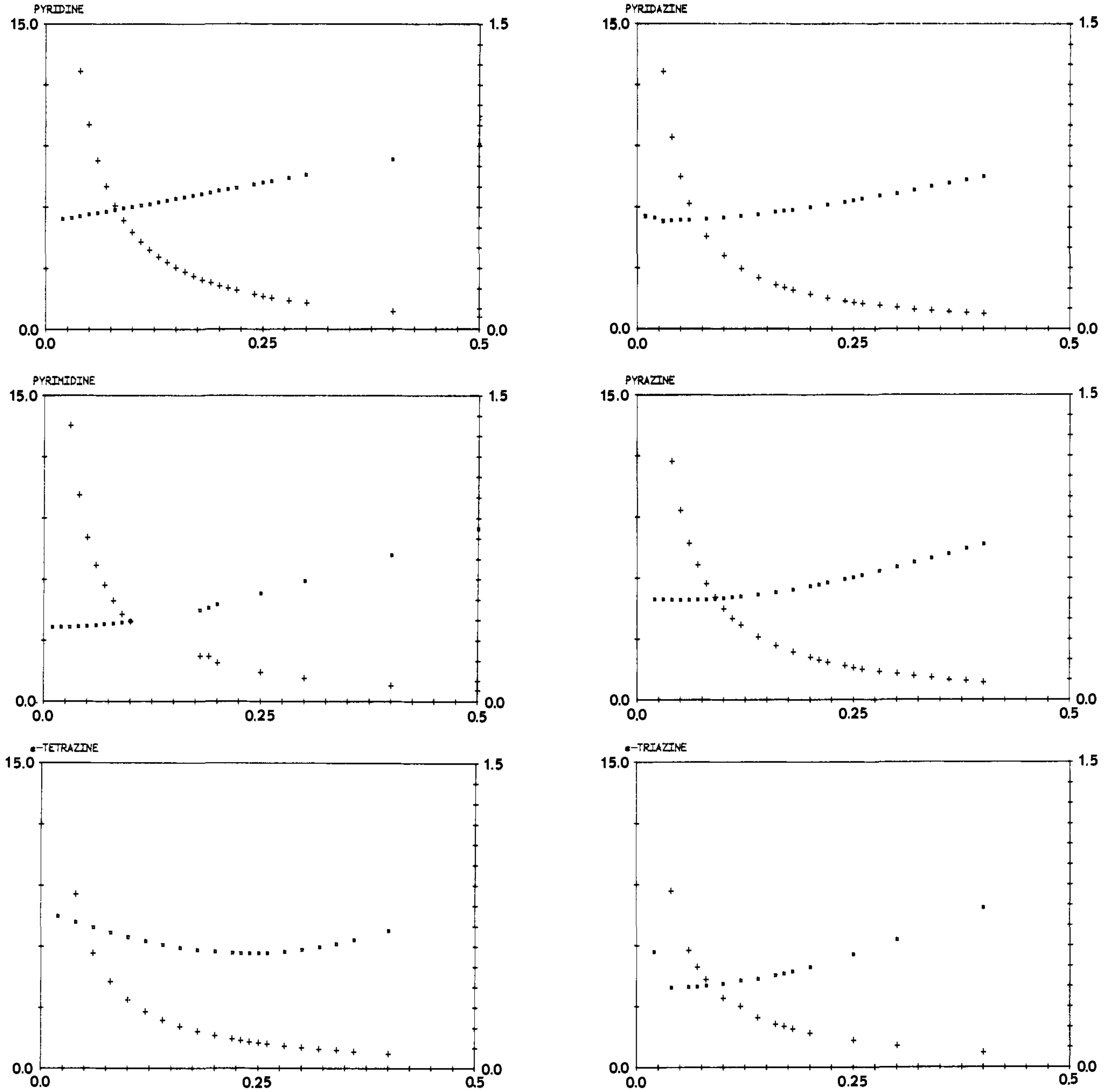

Figure 2. The lone-pair electron site charges and the fit to the calculated electrostatic potential around the molecules vs. the nitrogen to lone-pair distance (Å). The left-hand scale gives $-q_{LP}$ in electron units (curve with + points); the right-hand scale gives σ in kJ mol^{-1} (curve with □ points).

for use in the lattice energy minimization, because the lattice sum converges more easily with smaller site charges. Table II shows site charges for all atoms, as well as the lone-pair site charges, for the model with the lone pair taken at 0.25 Å out from nitrogen.

Table II shows the expected behavior of the goodness of fit indices, σ and s. The population analysis atomic site charges give a significantly less accurate description of the electric potential than the NLP potential-derived charges. Inclusion of lone-pair sites in the LP model further significantly improves the fits to the electric potential. The values of σ and s for the LP model are generally as good or better than the fits obtained by Cox and Williams[9] to a variety of smaller nonaromatic molecules.

The molecule which shows the greatest improvement of fit to the calculated electric potential in going from the NLP to the LP model is *s*-tetrazine. This was consistent with the above-mentioned early difficulties in predicting the crystal structure of *s*-tetrazine with a NLP model. Pyridazine also shows a large improvement going from the NLP to the LP model. Pyridine, pyrimidine, pyrazine, and *s*-triazine are fitted somewhat better by the NLP model, but nevertheless show further improved fits for the LP model. Note that the fits are uneven by the PA and NLP models, but it is favorable that all molecules considered are about equally well fitted by the LP model.

It appears from Figure 2 and Table II that in all of the molecules considered except tetrazine the electrostatic effect at the nitrogen could be approximated by a point dipole[26] located on the nitrogen, since the optimum lone-pair distance is short and the sum of the nitrogen and lone pair charges is nearly zero. For *s*-tetrazine there seems to be a significant extension of the lone pair away from the nitrogens. Sanford and Boyd[17] used a lone-pair model at a distance of 0.7 Å to calculate the molecular reorientation barrier in the pyrazine crystal.

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(26) A point dipole as considered here is an electrically neutral site in space which gives rise to a surrounding anisotropic electric potential due to its dipole moment. A distributed dipole is a set of two sites in space each having an electrical charge but each site itself having no dipole moment. The distributed dipole moment of the two sites is in the direction of the site–site vector and has a magnitude equal to one-half of the difference between the site charges multiplied by the intersite distance. As a special case the sum of the site charges may be zero.

Reynolds[15] used point dipoles at nitrogen and in the C–H bond. He used a value of 2.2 D obtained from NQR measurement of the electric field gradient at the nitrogen nucleus in pyridine.[27a] He obtained a fit for the crystal structure of pyrazine that is comparable to the present LP model. Table II shows that the LP model has an effective distributed nitrogen to lone-pair dipole of 1.93 for pyrazine, rather close to the above point dipole value. The other distributed dipoles range in value from 1.44 to 1.94. Gamba and Bonadeo[19] further allowed a variable location for the point dipoles of their model. Hirshfeld[27b] has proposed a general atomic multipole model for representation of the molecular charge distribution.

The LP model has an important advantage of computational simplicity over point multipole models. As an extension of the atom–atom model, the lone-pair site is simply treated as a dummy atom having isotropic electrostatic interactions. In contrast, the point multipole model requires additional bond-centered sites, and the general formulas for the anisotropic interaction of higher multipoles are more complex (see Burgos and Bonadeo,[28] for example).

Table III shows results of molecular packing analyses of the crystal structures of the azabenzenes which have been determined experimentally. Crystal data are given in Table I. Five of the six molecules considered here have known crystal structures; there are two known crystal forms of *s*-triazine.[29] The transition from the room-temperature α form to the low-temperature β form occurs at 198.07 K with a heat of transition[30] of 4.6 kJ mol^{-1}. In the MPA calculations all parameters not fixed by the observed space group symmetry were varied simultaneously to find the minimum of the lattice energy. At the final minimum energy of the structures the Hessian was always positive definite, but not necessarily at the observed structure. To indicate the importance of including the effects of the electric charge distribution in the molecules, a no-charge (NC) model was subjected to MPA as well as the PA, NLP, and LP site charge models.

Table III indicates that the poorest fits to the observed crystal structures were given by the NC and PA models. For several structures the NC model was actually superior to the PA model. The NLP model generally gives results of intermediate quality, while the LP model gives the best results.

For pyrimidine the LP model is clearly superior. It is the only model which has a positive definite Hessian matrix at the observed structure. The calculated lattice energy is slightly greater than the reported observed value.

Pyrazine also indicates a clear superiority for the LP model. Again, only this model has a positive definite Hessian at the observed structure. The calculated lattice energy is slightly less than either of the two reported observed values.

Table III. Differences between the Predicted Crystal Structure and the Observed Structure with the Different Charge Site Models[a]

crystal/ obsd energy	quantity	NC	PA	NLP	LP
pyrimidine	Δa	0.95	−1.04	−0.71	−0.01
48.8[44]	Δb	0.14	0.02	0.40	0.23
	Δc	−0.27	0.38	0.01	−0.17
	θ	19.8	16.9	8.7	2.7
	t	0.18	0.15	0.18	0.06
	energy at obsd struct	−35.8	−61.5	−54.7	−55.3
	negative eigenvalues	2	1	1	0
	energy at calcd struct	−40.5	−64.5	−56.7	−56.4
pyrazine	Δa	0.17	0.30	−0.43	0.22
63.6[45]	Δb	−0.29	0.88	−0.13	−0.14
53.6[15]	Δc	0.62	−1.20	0.75	0.05
	θ	22.5	22.4	22.5	1.7
	energy at obsd struct	−34.8	−62.6	−43.3	−51.9
	negative eigenvalues	1	1	1	0
	energy at calcd struct	−39.6	−69.7	−46.2	−52.8
s-triazine	Δa	0.31	−0.10	0.04	−0.01
(α form)	Δc	−0.29	−0.15	−0.48	−0.24
43.1[46]	energy at obsd struct	−36.3	−56.5	−57.6	−53.6
	negative eigenvalues	0	0	0	0
	energy at calcd struct	−38.3	−57.0	−59.7	−54.1
s-triazine	Δa	0.25	0.39	0.32	0.36
(β form)	Δb	−0.05	−0.02	0.11	−0.07
	Δc	−0.06	0.04	−0.30	−0.06
	$\Delta\beta$	−3.6	4.1	2.3	3.2
	θ	12.9	6.9	8.8	7.1
	t	0.11	0.13	0.10	0.10
	energy at obsd struct	−36.1	−56.2	−57.1	−53.7
	negative eigenvalues	1	0	0	0
	energy at calcd struct	−38.4	−57.0	−59.7	−54.2
s-tetrazine	Δa	0.44	−1.31	−1.05	0.39
	Δb	−0.39	2.49	1.25	0.46
	Δc	0.36	−0.03	0.44	−0.44
	$\Delta\beta$	−2.6	5.00	2.9	8.3
	θ	12.0	39.5	30.9	18.4
	energy at obsd struct	−28.2	−41.5	−44.7	−58.8
	negative eigenvalues	1	1	2	0
	energy at calcd struct	−33.0	−66.0	−61.5	−61.3

[a] Δa, Δb, Δc, and $\Delta\beta$ are the predicted shifts in the lattice constants (Å, deg) obtained by minimizing the lattice energy (kJ mol^{-1}); θ and t are the predicted molecular rotation (deg) and translation (Å) in the unit cell. The number of negative eigenvalues listed refers to the Hessian matrix of the second derivatives of the lattice energy with respect to the structural variables. NC = no-charge model; PA = population analysis net atomic charges; NLP = potential-derived net atomic charges; and LP = potential-derived site charges including both atomic and lone-pair electron sites. The site charges for the NLP and LP models were scaled by a factor of 0.82 from the values given in Table II (see text).

The α form of *s*-triazine has high symmetry and is relatively easy to predict with any of the models. In this case the PA model is about as good as the LP model. The calculated lattice energy is larger than the reported observed value. The β form, even with

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its lower symmetry, is also relatively easy to predict. Again, the PA model is nearly as good as the LP model. The LP model alone has the correct ordering of the energies of the two crystal forms, as contrasted to the other three models, but the predicted heat of transition is too low. Rae[16] calculated the energy of transition as 1.0 kJ mol^{-1} at absolute zero.

The crystal structure of *s*-tetrazine is the most difficult to predict and provides the most stringent test of the model for the molecular charge distribution. The PA and NLP models are poor; even the LP model is not as good as we would like. Surprisingly, the NC model is about as good as the LP model in its prediction. However, the NC model has a negative eigenvalue of the Hessian at the observed structure, and also the calculated energy appears to be too small.

Overall the LP model is the best of the four tested. Since in this work no attempt to optimize this model was made, it is likely that further improvement is possible. Since an important overall goal is to obtain transferability of the model parameters, a wider range of nitrogen-containing molecules should be considered in such an optimization. Another important overall goal is to allow the model to be applied to large molecules, even as large as proteins. The site-charge model has an advantage of computational simplicity to allow treatment of such larger molecules.

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Registry No. Pyridine, 110-86-1; pyridazine, 289-80-5; pyrimidine, 289-95-2; pyrazine, 290-37-9; *s*-triazine, 290-87-9; *s*-tetrazine, 290-96-0.

Vibrational Frequencies of the HCCN Molecule. A Near Degeneracy between Bent Cyanocarbene and Linear Allene-Related Geometries

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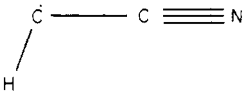
Abstract: The geometrical structure and vibrational frequencies of the ground triplet electronic state of HCCN have been examined at a wide range of levels of ab initio electronic structure theory. The potential energy surface of HCC bending is very flat for HCCN owing to a competition between linear allene $H\dot{C}{=}C{=}\dot{N}$ and bent carbene $H\ddot{C}C{\equiv}N$ valence structures. Evidence is presented that both the restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock (UHF) methods treat this potential surface in a somewhat uneven manner. When the effects of electron correlation are included, however, RHF- and UHF-based methods converge to a similar set of structural and energetic predictions. The most reliable levels of theory suggest that HCCN is a quasi-linear molecule, with θ_e(HCC) ≈ 138° and a barrier to linearity of only about 2 kcal/mol.

The first experimental studies of the HCCN triplet ground state were made via electron paramagnetic resonance (EPR) technique.[7–9] These results were interpreted in terms of a linear carbene model, as was considered natural[1,2] during the 1960s. However, in their landmark 1970 EPR study of CH_2 (declaring a substantially bent triplet ground state), Wasserman, Yager, and Kuck[5] comment briefly on HCCN. They note first that the nonlinearity of CH_2 might well be expected to carry over to cyanocarbene.



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This introduction notwithstanding, Wasserman states[5] that "the attempts we have made to examine $H\dot{C}CN$ in a variety of matrices at 4 K have only given spectra corresponding to *E* (zero field splitting parameter) = 0 thus supporting the linear form." In assessing these EPR data, Dendramis and Leroi[6] note that matrices may impose barriers to rotation, and the inability to detect rotation does not necessarily mean that the molecule must be linear. Hyperfine structural data, not yet available for HCCN, are necessary before a definitive pronouncement about the geometry can be made.

The most detailed experimental data available for HCCN come from the matrix isolation infrared study of Dendramis and Leroi.[6] They assigned five fundamental frequencies for DCCN and four each for HCCN, $HC^{13}CN$, and $HCC^{15}N$. Dendramis and Leroi (DL) state specifically that their failure to observe more than five vibrational fundamentals does not prove the linearity of HCCN. However, they do eventually conclude that the molecule is linear (with the allene-like structure **2**) on the basis of their normal-coordinate analysis. For example, the observed frequency at 1735

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