1122. *Bond Angles in Nitrogen-containing Heterocyclic Molecules.*

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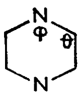
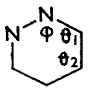
It is shown that a simple valence-force field is adequate to explain the observed bond angles in the series of heterocyclic aromatic molecules derived from benzene by replacement of 1, 2, 3, or 4 CH groups by nitrogen atoms.

When one of the CH groups in benzene is replaced by a nitrogen atom, to give pyridine, there are interesting changes in the ring angles. The CNC angle drops from 120° to 117°, the NCC angle increases to 124°, and the CCC angles drop to about 118°. Similar changes occur in all other molecules of this type, in which there may be more than one such aza-replacement. Kim and Hameka[1] recently collected experimental results for the six molecules here formulated. These are shown in the Table the notation being as marked in the formulæ. Kim and Hameka tried to explain these deviations from 120° in terms of repulsions from the lone-pair electrons on the nitrogen atoms, using wave-mechanical methods to calculate the total energy of the σ-bonds and lone-pair electrons. Their results (see Table) show that the attempt was only partially successful; as they pointed out, it failed most significantly for pyridine and pyrimidine, where all ring angles at the carbon atoms were predicted to exceed 120°, although experimentally several of these angles are actually less than 120°. It is the purpose of this paper to show that an adequate explanation of the complete pattern of bond angles can be obtained by a simpler method. In every case this method gives the correct sign of the deviation from the "ideal" value of 120°, and the maximum error is just over 2°. This is about one-third of the Kim–Hameka error; and the mean error of 1·2° is not much greater than the experimental uncertainty in some of the measurements.

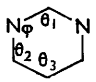
Pyridine



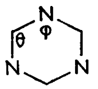
Pyrazine



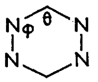
Pyridazine



Pyrimidine



s-triazine



s-tetrazine

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[1] Kim and Hameka, *J. Amer. Chem. Soc.*, 1963, **85**, 1398.

Calculated and observed valence angles.

Angle	Kim–Hameka value[1]	Experimental value[1]	Present paper	Angle	Kime–Hameka value[1]	Experimental value[1]	Present paper
	Pyridine				Pyrimidine		
ϕ	110°	117°	115·0°	ϕ	111°	115°	115·0°
θ_1	121	124	124·4	θ_1	124	128	128·7
θ_2	122	118·5	119·4	θ_2	125	123	121·3
θ_3	123	118	117·0	θ_3	124	116	118·6
	Pyrazine				1,3,5-Triazine		
ϕ	112	115	112·6	ϕ	114	113	114·4
θ	124	122·5	123·7	θ	126	127	125·6
	Pyridazine				1,2,4,5-Tetrazine		
ϕ	113		120·1	ϕ	115	116	116·3
θ_1	124		124·0	θ	130	127	127·5
θ_2	123		116·9				

METHOD

Let us suppose that there is a " natural " valency angle for an aromatic carbon and nitrogen ring atom. For carbon this angle must presumably be 120°, or close to it, as the situation in ethylene makes clear. For nitrogen it will be less than this, and may easily be not greatly different from the ammonia angle. We do not know this natural angle, and so we call it ϕ_0, which we write in the more convenient form $\phi_0 = 120° - \beta$, where $0 < \beta < 13°$. Further, let us suppose that there are force constants k_C and k_N which apply to the bending of these angles, so that the potential energy of a molecule of this kind is the sum of an appropriate number of terms $\frac{1}{2}\, k_C\Delta\theta^2$ and $\frac{1}{2}k_N\Delta\phi^2$, where $\Delta\theta = \theta - 120°$, and $\Delta\phi = \phi - \phi_0 = \phi - (120° - \beta)$. We are supposing that k_C is the same for the bending of CCC, CCN, and NCN angles; and similarly for k_N. The actual numerical values of k_C and k_N are not known, but fortunately only their ratio will be needed, and the final numerical results do not appear to be very sensitive to this ratio, which must evidently be in the neighbourhood of unity. We shall also suppose that in all these molecules, all C–C bonds are of length *a*, all C–N bonds of length *b*, and all N–N bonds of length *c*. This is obviously an approximation, but the accurate analysis of pyridine by Bak, Hansen, and Rastrup-Anderson[2] shows that it is not seriously wrong. A more thoroughgoing study of any one particular molecule would require us to be more precise about these lengths, but, as will appear below, this does not seem to be necessary in order to reproduce the essential features of the experimental values in the Table.

Our method is simply that of writing the total potential energy of each molecule in terms of its bond angles, and then choosing these angles so that the energy is minimized, subject, of course, to the necessary geometrical constraints imposed by the fact that the molecule is a closed, planar, irregular hexagon.

Three of the set of six molecules (pyrazine, 1,3,5-triazine, and 1,2,4,5-tetrazine) present much less difficulty than the others. This is because their symmetry is such that only one geometrical constraint is required, whereas the other three molecules require two such constraints. As a result the relative values of the bond lengths *a,b,c* play no part in the final predictions. We shall therefore deal with these molecules first, and use them to estimate the unknown angle β. After that, with the same parameters, we shall turn to the three more complicated molecules.

Let us consider the triazine as an example of the first set of molecules. With the angles shown the total potential energy is

$$W = \tfrac{3}{2}\, k_C\Delta\theta^2 + \tfrac{3}{2}k_N\Delta\phi^2, \tag{1}$$

and the only restrictive geometrical condition is that $\Delta\theta + \Delta\phi = \beta$. We write this in the form

$$f(\Delta\theta,\, \Delta\phi) \equiv \Delta\theta + \Delta\phi - \beta = 0. \tag{2}$$

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[2] Bak, Hansen, and Rastrup-Anderson, *J. Chem. Phys.*, 1954, **22**, 2013.

The minimization of W subject to condition (2) is equivalent to the unrestricted minimization of

$$U = W - 3\lambda f \tag{3}$$

where λ is a Lagrange undetermined multiplier, and the factor 3 is inserted for numerical convenience. The defining equations for the minimum now are $\partial U/\partial(\Delta\theta) = 0 = \partial U/\partial(\Delta\phi) = \partial U/\partial\lambda$. So

$$k_C\Delta\theta - \lambda = 0,$$
$$k_N\Delta\phi - \lambda = 0,$$
$$\Delta\theta + \Delta\phi = \beta.$$

Thus

$$\Delta\theta = \frac{\beta}{(1 + k_C/k_N)}; \; \Delta\phi = \frac{k_C}{k_N}\frac{\beta}{(1 + k_C/k_N)}. \tag{4}$$

The distortions depend only on β and the ratio k_C/k_N.

In a similar way, for 1,2,4,5-tetrazine

$$\Delta\theta = \frac{2\beta}{(1 + 2k_C/k_N)}; \; \Delta\phi = \frac{k_C}{k_N}\frac{2\beta}{(1 + 2k_C/k_N)}; \tag{5}$$

and for pyrazine

$$\Delta\theta = \frac{\beta}{(2 + k_C/k_N)}; \; \Delta\phi = \frac{k_C}{k_N}\frac{\beta}{(2 + k_C/k_N)}. \tag{6}$$

We can now use the equations (4)—(6) to obtain the best values of our fundamental parameters β and k_C/k_N. A least-squares fit shows that the choice is not at all critical, provided that, for any chosen k_C/k_N, the appropriate β is selected. In view of this, and our earlier comment that k_C and k_N must not differ greatly, we have adopted the simple equality $k_C = k_N$. This gives

$$\beta = 11{\cdot}18°, \tag{7}$$

which is a very satisfying value, lying in the range previously mentioned, and corresponding to a " natural " valency angle of 109° in nitrogen, when embedded in an aromatic ring system. More refined calculations are possible, but are not worth making till the experimental angles are better known. We therefore adopt the value in (7). The Table shows that even with this simple theory the greatest error in a carbon angle is less than 1·5°.

We now turn to the three more complicated molecules, taking pyrimidine as our example. The total potential energy W is written, as in (1). The geometrical constraints, however, are now two in number: (i) that the sum of the internal angles of the ring is 720°, and (ii) that, in terms of the diagram, the bottom vertex lies directly below the top one. This means that

$$b \sin \tfrac{1}{2}\theta_1 - b \sin (\tfrac{1}{2}\theta_1 + \phi) - a \sin \tfrac{1}{2}\theta_3 = 0.$$

We now have to minimize a function U similar to (3) except that there are two Lagrange multipliers instead of only one. After some reduction the results are

$$\Delta\theta_1 = x + 3y; \; \Delta\theta_3 = x - \frac{a}{b}y;$$

$$\Delta\theta_2 = x; \; \Delta\phi = \frac{k_C}{k_N}(x + 2y); \tag{8}$$

where

$$\left(4 + \frac{2k_C}{k_N}\right)x + \left(3 - \frac{a}{b} + \frac{4k_C}{k_N}\right)y = 2\beta;$$

$$\left(3 - \frac{a}{b} + \frac{4k_C}{k_N}\right)x + \left(9 + \frac{a^2}{b^2} + \frac{8k_C}{k_N}\right)y = 2\sqrt{3}\left(\frac{a}{b} - 1\right) + 4\beta. \tag{9}$$

In (9) we have omitted terms of the second order of small quantities, and have treated β for this purpose as if it were small, of first order.

We have already agreed to put $k_C/k_N = 1$. This simplifies (9), and allows us to solve the equations. Once again, correct to the first order of small quantities:

$$x = \frac{\beta}{6} + \frac{\sqrt{3}}{6}\left(\frac{1}{b} - \frac{a}{b}\right) - \left(1 - \frac{a}{b}\right)\frac{\beta}{18};$$

$$y = \frac{\beta}{6} - \frac{\sqrt{3}}{6}\left(1 - \frac{a}{b}\right) + \left(1 - \frac{a}{b}\right)\frac{\beta}{36}.$$

If we neglect the difference $(a - b)$ between a C–C bond and a C–N bond, then we find that $\Delta\theta_1 = 7{\cdot}5°$, $\Delta\theta_2 = 1{\cdot}8°$, and $\Delta\theta_3 = 0°$. These are in the correct sequence, but not good enough. To get a better result we must include the difference between a and b. So, referring to the experimental values,[2] we take

$$a = 1{\cdot}395,\ b = 1{\cdot}342,\ c = 1{\cdot}289, \text{ all in Å}. \qquad (10)$$

The value of c is not found in ref. 2, but has been assumed on the ground that the C–C, C–N, and N–N bonds should be in simple arithmetical progression. It can be seen that the precise value of the N–N bond length c occurs only in pyridazine, for which, unfortunately, there are as yet no experimental measurements. With these values (10) we are led to our final pyrimidine displacements $\Delta\theta_1 = 8{\cdot}7°$, $\Delta\theta_2 = 1{\cdot}3°$, and $\Delta\theta_3 = -1{\cdot}4°$. The improvement in $\Delta\theta_3$, which now has a negative value, is noteworthy.

A similar analysis gives the values for pyridine and pyridazine shown in the Table. Since no experimental values exist for the latter molecule, our values may be treated as theoretical estimates, not likely to be more than 2° in error.

DISCUSSION

It is obvious from the Table that the calculated angles reproduce all important features of the observed values, including the contraction of the angles θ_2, θ_3 in pyridine, θ_2 in pyridazine, and θ_3 in pyrimidine. The mean deviation between the experimental and calculated values in the Table is only 1·2°. It is interesting that the original force-field, without taking account of the difference in C–C and C–N bond lengths, would not by itself give negative $\Delta\theta$-values for any of the carbon atoms. This may partly explain why Kim and Hameka always obtained positive $\Delta\theta$-values, and also why they found more satisfactory results for the three molecules (1,3,5-triazine, 1,2,4,5-tetrazine, and pyrazine) for which, as we have shown, the actual bond lengths do not affect the geometrical constraints. It appears that it is this fact, rather than their greater symmetry, which is significant for this purpose. It will also be noticed that the CNC angle is consistently less than 120°, and usually about 115—116°, with the single exception of pyridazine, where it is as great as 120·1°. This exception arises from the assumed value of the N–N distance c; by being shorter than N–C or C–C this tends, in this case, to open out the bond angles at the nitrogen atoms.

Better agreement than the present could presumably be obtained by more careful attention to some of the factors that we have either neglected or averaged. In a general discussion, however, this does not seem worthwhile.

Finally, since, in these planar molecules, the force constants k_N and k_C are governed primarily by the σ-bonds, and hardly at all by the π-bonds, we are in effect attributing the variations in ring angle to the σ-bond framework rather than to the π-electrons. This is an eminently reasonable situation.

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