*Inorganic Chemistry*

# Conformational Analysis of Coordination Compounds. II. Substituted Five-Membered Diamine Chelate Rings

BY J. R. GOLLOGLY AND C. J. HAWKINS

The conformations of chelate rings involving ethylenediamine, propylenediamine, and N-methylethylenediamine have been studied by detailed *a priori* conformational energy calculations. It has been found that for ethylenediamine there are a number of energetically equivalent symmetrical and unsymmetrical "minimum-energy" conformations. This is in contrast with the presently accepted view that the ring is limited to two mirror-image symmetrical conformations. The substituted ethylenediamine chelate rings with the substituent axial possess a different range of conformations which does not include a symmetrical conformation. The energy differences between the equatorial and axial conformations have been computed using Hill's, Bartell's, and Mason and Kreevoy's nonbonded interaction energy expressions in order to compare the results obtained when typical low-, medium-, and high-energy expressions are employed. The results regarding the geometrical parameters are in agreement with data determined by X-ray structural studies.

The interpretation of circular dichroism and infrared and nuclear magnetic resonance spectra of metal complexes containing chelate rings is somewhat dependent upon a knowledge of the geometry of the various conformations of these rings and of the energy differences between the conformations. Predictions of stereospecificity due to conformational preferences are also dependent upon this information. Since 1959, the solution of these problems has mainly been based on the conclusions drawn by Corey and Bailar in their investigations of metal–ethylenediamine and other ring systems.[1] However, more recently there have been many developments in the conformational analysis of organic molecules which have enabled *a priori* calculations of energy terms to be attempted on a more rigorous basis, and, consequently, it seemed worthwhile to reinvestigate the fundamental chelate ring systems. In this paper the results are presented of a study of the conformations of ethylenediamine and methyl-substituted ethylenediamine in complexes of the general type given in Figure 1.

On the basis of a primitive conformational analysis, Corey and Bailar[1] had concluded that the five-membered ethylenediamine chelate ring exists in two enantiomeric skew conformations which correspond to energy minima. These conformations were symmetric in the sense that the two carbon atoms of the ring were equidistant but on opposite sides of the plane of the coordinate bonds. The above workers, as well as subsequent workers in the field,[2] have assumed that the possible conformations of substituted ethylenediamine rings are identical with these, irrespectively of whether the substituents are axial or equatorial.

The method used by Corey and Bailar merely involved inspection of the torsional and bending energy terms to determine the possible ring conformations, followed by a routine calculation of the van der Waals term based on these conformations. Such an approach is appropriate only in situations where the van der Waals

energy from interactions between substituents on the chelate ring and other atoms in the complex molecule is relatively unimportant because it does not allow for any effect of van der Waals interactions on the actual ring conformations. In this study, the molecular geometry was varied in such a way as to minimize the sum of the various conformational energy terms.

## Energy Terms

**Torsional Energy.**—Torsional barriers were estimated by considering model organic systems. The barrier to rotation about the C–C bond in ethane has been found experimentally to be 2.8 kcal mol⁻¹ and this is only slightly altered when an H atom is replaced by a methyl group as in propane where the value is 3.3 kcal mol⁻¹.[3] Thus the barriers about the C–C bonds in ethylenediamine and propylenediamine would be very similar. In fact, a wide range of substituted ethane molecules have barriers of the order of 3 kcal mol⁻¹ for their C–C bonds. On this basis, it would seem reasonable to accept this value as being of the right order for the ethylenediamine and the substituted ethylenediamine chelates.

The barriers to rotation about C–N bonds are generally slightly lower in value. By comparison with the observed barrier[3] of 1.9 kcal mol⁻¹ for methylamine, a value of 2 kcal mol⁻¹ has been selected as an approximate value for bonds of this type in the chelates.

Unfortunately there is no comparable experimental information regarding the torsional barriers about the coordinate bonds. Some simplifying assumptions about these barriers may be made if, for the case of substituents like ammonia or an amine, we use a term of the type

$$E_t = \frac{1}{2}V'(1 + \cos 3t)$$

to account for the torsional behavior of one coordinate bond with respect to the three substituents of a coordinated atom (see Figure 2). The torsional energy

---

(1) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(2) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967); F. Woldbye, *Proc. Roy. Soc.* (London), **A297**, 79 (1967).

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 140.
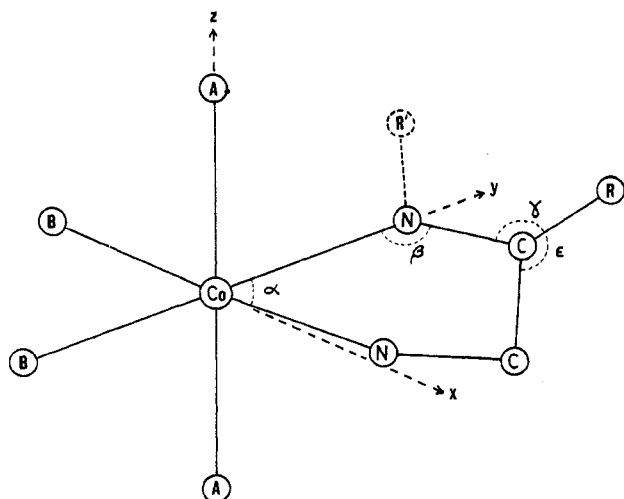
Figure 1.—Complex under investigation located in the coordinate system.

about a coordinate bond, which derives from four such terms, is given by

$$E_t = \sum_{i=1}^{4} {}^1/_2 V'_i [1 + \cos 3(t + (i - 1)90)]$$

For the complexes under investigation, the barriers $V'_i$ would be of the same order of magnitude, and, therefore, the summation would approach zero.
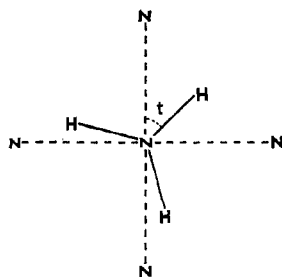


Figure 2.—Torsional arrangement about a Co–N bond.

**Angle-Bending Energies.**—These terms were calculated using the normal Hooke's law relationship

$$E_\theta = {}^1/_2 k_\theta (\Delta\theta)^2$$

where $k_\theta$ is the force constant for bending the angle and $\Delta\theta$ is the deviation from the normal undistorted bond angle.[4] Little information is available regarding the bending force constants for the individual bond angles of the five-membered diamine chelate rings. However, Condrate and Nakamoto have shown that, for glycine, chelation produces little change in the force constants associated with the bond angles of the free glycinate ion.[5] Consequently, the angle-bending force constants for the chelated diamines were assumed to be similar to those of the free ligand. However, as these are not available, the CCC and CCN angles of the diamines were taken to have force constants of the same order of

magnitude as those of similar angles in organic systems: 100 kcal mol$^{-1}$ radian$^{-2}$.[6]

It would appear that the angles MNC and MNH have bending force constants which are much less than those discussed above,[5,7] and a value of 40 kcal mol$^{-1}$ radian$^{-2}$ has been assumed for angles of this type. The values obtained by Nakagawa and Shimanouchi[7] for the force constants associated with $\angle$NCoN are too high to be consistent with the distortions of this angle observed in X-ray structures. A value of 60 kcal mol$^{-1}$ has been assumed for these calculations. The force constants calculated for $\angle$NCoCl are less than those for $\angle$NCoN,[7] and thus a value of 40 kcal mol$^{-1}$ has been selected for this angle.

**van der Waals Energies.**—There is a large number of expressions in the literature for calculating nonbonded interaction energies.[8] These range from the low-energy interaction expressions of Hill[9] to the high-energy expressions of Mason and Kreevoy[10] which were used by Corey and Bailar.[1] In recent years the conformational energy calculations of chelate rings have mainly been based on Hill's equations.[2] However, although relatively good agreement between experimentally determined and computed values of conformational energy differences has been found when the low-energy terms have been used for some organic ring systems,[8] there is some support for using higher energy expressions.[11] In this paper we have computed energy differences using Hill's,[9] Bartell's,[12] and Mason and Kreevoy's[10] equations describing the variation of the van der Waals energies with interatomic distance. These are typical of the low-, medium-, and high-energy expressions, respectively, and thus we have been able to compare the conclusions regarding the geometries and energies of the conformations for the complete range of nonbonded interaction energy expressions. van der Waals curves for the most important interactions are given in Figure 3.

**Bond Length Distortion Energy.**—The energies associated with bond length distortion were estimated using the usual equation $E_l = {}^1/_2 k_l (\Delta l)^2$, where $k_l$ is the force constant for bond length distortion and $\Delta l$ is the change in the bond length from the normal length.[4] The following undistorted bond lengths (in Å) were assumed: Co–N, 2.00; C–C, 1.54; C–N, 1.47; C–H, 1.10; N–H, 1.00; Co–Cl, 2.30. The work of Condrate and Nakamoto[5] suggests that, for glycine, chelation also does not alter the value of the bond-stretching force constants of the ligand. Thus, C–C and C–N bonds of the diamine rings were assigned force constants with values of 648 and 488 kcal mol$^{-1}$ Å$^{-2}$ by comparison with the force constants usually found for these bonds in organic molecules.[5,6] The value for the Co–N bond

(4) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, pp 525, 526.

(5) R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2540 (1965).

(6) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, pp 447, 448.

(7) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1707 (1966).

(8) See, for example, J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(9) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(10) E. A. Mason and M. M. Kreevoy, *J. Am.Chem. Soc.*, **77**, 5808 (1955).

(11) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967).

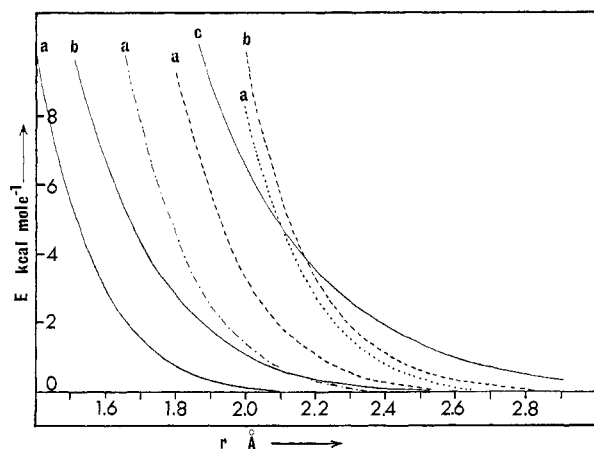(12) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

Figure 3.—van der Waals energy curves for the significant interactions: a, Hill; b, Bartell; c, Mason and Kreevoy; H–H, —; C–H, --; N–H, -·-; Cl–N, ···.

distortion was taken to be the same as that found[7] for $Co(NH_3)_6^{3+}$.

## Geometrical Model

For the purposes of these investigations, the complex molecule was placed in a right-handed Cartesian-coordinate system with the metal atom at the origin and the two coordinate bonds lying in the $xy$ plane (see Figure 1). For a given set of bond lengths, the conformation of the chelate ring is most usefully defined by the unique set of parameters $\alpha$, $\beta$, $Z_1$, and $Z_2$. In terms of the diamine ring shown in Figure 1, $Z_1$ and $Z_2$ are the $z$ coordinates of the two ring carbon atoms $C(1)$ and $C(2)$, and $\alpha$ and $\beta$ are the two ring angles $\angle N(1)CoN(2)$ and $\angle CoN(1)C(1)$. (The other ring angles remain unspecified but can be determined for any conformation.) The geometry of any substituent to the ring is defined by the necessary bond lengths and bond angles. The positions of groups A and B are defined by the Cartesian coordinates of the coordinated atoms (*e.g.*, $x_A$, $y_A$, $z_A$).

To complete a unique description of the system, some comment must be made about the orientation of rotating groups of the types R (or R′) = $CH_3$– and A, B = $NH_3$. Since the staggered and eclipsed orientations of such a group, R (or R′), with respect to the ring will probably differ in torsional energy by about 3 kcal, it has been assumed that R will remain in a staggered orientation. Since, as noted previously, the torsional barrier affecting the orientation of A will probably be very small, A has been allowed to orient itself freely so that its van der Waals interactions with the rest of the system are minimized.

Under this model, variations in the system are produced by varying bond lengths, bond angles, $Z_1$, $Z_2$, and ligand coordinates. Any physically possible structure may be specified by an appropriate choice of these parameters.

## Energy Calculations

Initially we are concerned with the range of possible conformations. For each set of ring parameters ($\alpha$, $\beta$, and the five bond lengths), the coordinates $Z_1$ and $Z_2$

were varied by first choosing a value of $Z_1$ and varying $Z_2$ through its entire range of possible values. A new value of $Z_1$ is then chosen and $Z_2$ is again varied. This process is repeated for all possible values of $Z_1$ until the complete range of possible conformations has been investigated. The precise ring conformations may be further altered by using different sets of ring parameters. This type of conformational variation was repeated for various sets of the remaining parameters to take into account distortions other than those associated with the ring skeleton. A computer was used to calculate the relevant interatomic distances, torsional angles, and bond angles for each structure defined in this way.

A survey of this type suggests that bond length distortion is energetically too unfavorable to be of significance in these calculations. Angle distortions outside the ring appear to be centered on only three angles for both the C-substituted ($\angle N(1)C(1)R$ ($\gamma$), $\angle C(2)C(1)R$ ($\delta$), and $\angle ACoN$) and N-substituted ($\angle CoN(1)R'$ ($\gamma'$), $\angle C(1)N(1)R'$ ($\epsilon'$), and $\angle ACoN$) ligands.

**Ethylenediamine Complexes.**—First, the situation where the van der Waals interactions are insignificant will be considered. In this case, the total conformational energy arises from the two terms $E_t$ and $E_\theta$ which may be evaluated for each conformation defined by the parameters $\alpha$, $\beta$, $Z_1$, and $Z_2$. For each set of values of $\alpha$, $\beta$, and $Z_1$, $Z_2$ has been varied through its entire geometrically possible range, specifying a range of conformations which corresponds to a range of values of $\omega$, the dihedral angle between the $N(1)C(1)C(2)$ and $N(2)C(2)C(1)$ planes. Therefore, for each set of $\alpha$, $\beta$, and $Z_1$, a set of graphs may be drawn expressing the relationship between $\omega$ and the three energy terms $E_t$, $E_\theta$, and $(E_t + E_\theta)$. These energy terms have been investigated for the following parameters: $\alpha = 84, 86, 88,$ and $90°$; $\beta = 104.5, 109.5, 114.5,$ and $119.5°$; $Z_1 = 0, 0.1, 0.2, 0.3, 0.4, 0.5,$ and $0.6$ Å. Typical graphs are shown in Figure 4.

The graphs of $E_t$ against $\omega$ are almost superimposable for all the above values of $\alpha$, $\beta$, and $Z_1$, implying that the value of the total torsional energy of the ring is nearly independent of the actual conformation of the ring (defined by $\alpha$, $\beta$, $Z_1$, and $Z_2$) and depends almost exclusively on the torsional arrangement about the C–C bond (defined by the secondary parameter $\omega$). Since the torsional energy term derives from the three significant torsional energies associated with the $N(1)C(1)$, $C(1)C(2)$, and $N(2)C(2)$ bonds, this result implies that if $Z_1$ and $Z_2$ are altered in such a way as to maintain a constant value of $\omega$, any increase in $E_t(N(1)C(1))$ caused by this change is accompanied by a compensating decrease in $E_t(C(2)N(2))$ and *vice versa*, leading to a constant value of $E_t$.

The implication of this result is of great significance. It follows from the above discussion that the torsional energies of symmetrical and unsymmetrical conformations of the type shown in Figure 5 will be very similar provided the torsional arrangements about $C(1)C(2)$ are the same in each case.
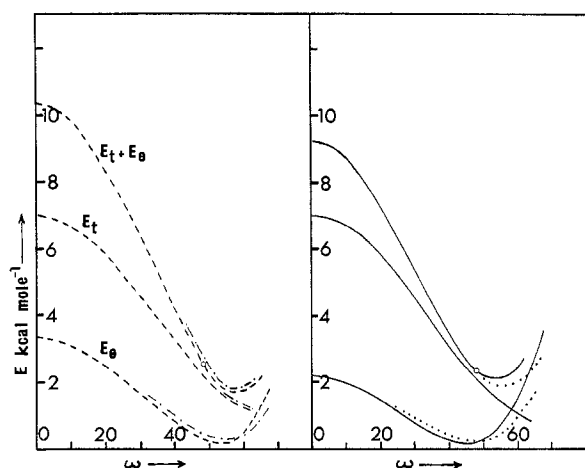
Figure 4.—Typical graphs illustrating variations of $E_t$, $E_\theta$, and $(E_t + E_\theta)$ with $\omega$: $\alpha = 86°$, $\beta = 109.5°$, $Z_1 = -Z_2$ (————); $\alpha = 89°$, $\beta = 109.5°$, $Z_1 = 0.0$ (······); $\alpha = 90°$, $\beta = 104.5°$, $Z_1 = -Z_2$ (——————); $\alpha = 90°$, $\beta = 104.5°$, $Z_1 = 0.0$ (—·—·—·—). The small circle marks a Corey and Bailar conformation.
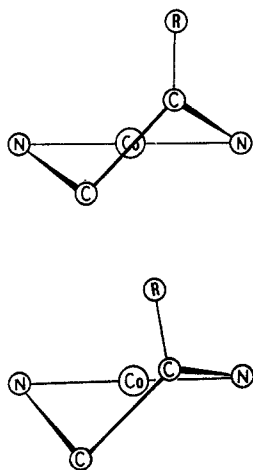




Figure 5.—Two energetically equivalent ethylenediamine–cobalt(III) chelate rings with identical values of $\omega$ but different sets of ($Z_1$, $Z_2$) corresponding to symmetrical and unsymmetrical conformations.

The effects of $\alpha$, $\beta$, $Z_1$, $Z_2$, and $\omega$ on $E_\theta$ were investigated in a similar way. In this case the energy term is strongly dependent on $\alpha$, $\beta$, and $\omega$ and, to a first approximation, independent of $Z_1$ and $Z_2$. The total ring-strain energy $(E_t + E_\theta)$ is, therefore, also dependent upon these three parameters and largely independent of $Z_1$ and $Z_2$.

Graphs of $(E_t + E_\theta)$ against $\omega$ show that for each set of $\alpha$, $\beta$, and $Z_1$ there are two energy minima separated by an energy barrier due mainly to torsional terms and bounded by an energy gradient derived from angle-bending energies. In the absence of significant van der Waals interactions, the ethylenediamine ring will exist in the conformations which have $(E_t + E_\theta)$ energy minima of lowest energy. These have been determined by the above procedure: relevant data are given in Table I. It is clear from the results that a whole range of symmetrical and unsymmetrical conformations correspond to a minimum ring-strain energy of $1.7 \pm 0.2$ kcal mol$^{-1}$.

TABLE I
SOME MINIMUM-ENERGY COBALT(III)
ETHYLENEDIAMINE CONFORMATIONS

| $\alpha$, deg | $\beta$, deg | $Z_1$, Å | $Z_2$, Å | $\omega$, deg |
|---|---|---|---|---|
| 90 | 104.5 | 0.1 | −0.6 | 56 |
| 90 | 104.5 | 0.1 | −0.7 | 57.5 |
| 90 | 104.5 | 0.2 | −0.5 | 55 |
| 88 | 109.5 | 0.1 | −0.5 | 47 |
| 88 | 104.5 | 0.2 | −0.6 | 62 |
| 88 | 104.5 | 0.4 | −0.4 | 61 |
| 86 | 109.5 | 0.0 | −0.7 | 55 |
| 86 | 109.5 | 0.1 | −0.6 | 53.5 |
| 86 | 104.5 | 0.4 | −0.4 | 60 |

Investigations show that, for the complexes considered in this paper, the van der Waals interactions of the ethylenediamine chelate ring with other groups in the molecule are very small ($<0.1$ kcal) when Hill's or Bartell's equations are used, and, consequently, the rings in these complexes will exist in the range of conformations predicted on the basis of the ring-strain energies alone. When the Mason and Kreevoy equation is used, such interactions become more significant and tend to limit this range of conformations.

**Propylenediamine Complexes.**—Although the following calculations will naturally be equivalent for both optical isomers of propylenediamine, throughout this paper we will consider only the $l$ isomer which has the $R$ absolute configuration.[13] The propylenediamine chelate ring possesses ring-strain characteristics which are identical with those of the ethylenediamine rings. However, in this case, the van der Waals term is significant and is of great importance in limiting the range of conformations available to the chelate ring.

The nonbonded interaction energies arise from the interactions of the methyl group with the groups A and B and with other atoms in the chelate ring. For each of the three different types of van der Waals equations being considered here, a value of $E_v$ has been calculated corresponding to the following sets of geometrical variables: $\alpha$, $\beta$, $Z_1$, $Z_2$ (varied as in the ethylenediamine system); $\gamma$, $\epsilon = 109.5$ and $114.5°$; and ($x_A$, $y_A$, $z_A$) = (0, 0, 2.0), (−0.1, −0.1, 2.0), (−0.2, −0.2, 2.0). For each set of geometrical variables, the total conformational energy has been determined as the sum of the van der Waals energy, the appropriate ring-strain energy, and the additional angle-bending energies arising from distortions which occur outside the ring to relieve the van der Waals interactions. Such an investigation reveals that the interactions of the group B (where B is, for example, $NH_3$, $H_2O$, $Cl^-$, $Br^-$) and also the interactions of the methyl group with other atoms in the chelate ring appear to be of no significance to these calculations.

For each set of variables ($\alpha$, $\beta$, $Z_1$, $x_A$, $y_A$, $z_A$), it is possible to draw a graph of the variation of total conformational energy with $\omega$ for each of the three van der Waals equations (see Figure 6). The preferred conformations are again determined by finding those whose energy

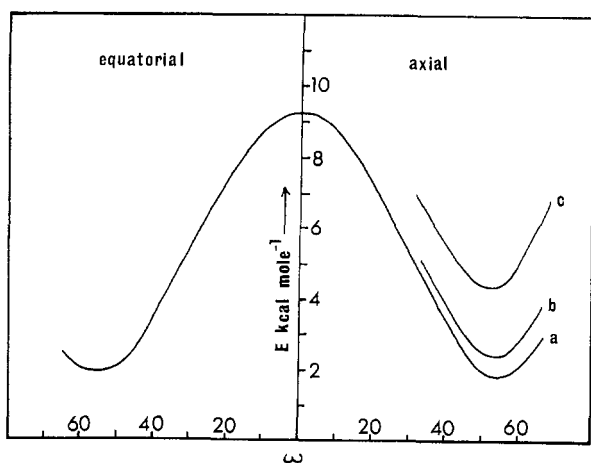(13) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

Figure 6.—Typical graphs of the variation of total conformational energy $E$ with $\omega$ for the complex $Co((R)\text{-pn})(NH_3)_4{}^{3+}$:  a, Hill; b, Bartell; c, Mason and Kreevoy.

minima lie at the lowest energy. The results are as follows.

When A is ammonia, using Hill's equation the minimum-energy $(1.8 \pm 0.1 \text{ kcal mol}^{-1})$ axial conformations include those with $\alpha = 90°$, $\beta = 104.5°$, $\gamma$ and $\epsilon = 109.5°$, $\omega = 57.5°$, $Z_1 = 0.0\text{Å}$, $Z_2 = -0.7$ Å, and $(x_A, y_A, z_A) = (0, 0, 2.0)$ or $(-0.1, -0.1, 2.0)$ and those with $\alpha = 86°$, $\beta$, $\gamma$, and $\epsilon = 109.5°$, $\omega = 55°$, $Z_1 = 0.0$ Å, $Z_2 = -0.7$ Å, and $(x_A, y_A, z_A) = (0, 0, 2.0)$ or $(-0.1, -0.1, 2.0)$. With Bartell's expressions, the minimum energy $(2.4 \pm 0.1 \text{ kcal mol}^{-1})$ conformations are identical with the above except that $(x_A, y_A, z_A)$ is forced toward $(-0.1, -0.1, 2.0)$. When Mason and Kreevoy's equations are employed, the minimum energy of 4.5 kcal mol$^{-1}$ is attained for $\alpha = 88°$, $\beta = 109.5°$, and $\gamma$ and $\epsilon = 114.5°$, $\omega = 48°$, $Z_1 = 0.0$ Å, $Z_2 = -0.6$ Å, and $(x_A, y_A, z_A) = (-0.1, -0.1, 2.0)$ or $(-0.2, -0.2, 2.0)$ and for $\alpha = 86°$, $\beta = 109.5°$, $\gamma$ and $\epsilon = 114.5°$, $\omega = 55°$, $Z_1 = 0.0$ Å, $Z_2 = -0.7$ Å, and $(x_A, y_A, z_A) = (0, 0, 2.0)$ or $(-0.2, -0.2, 2.0)$. For the complex where A is the chloride ion, using Hill's equation the same conformations to the above correspond to the minimum energy of $2.0 \pm 0.1$ kcal mol$^{-1}$ except that $(x_A, y_A, z_A)$ is distorted to $(-0.1, -0.1, 2.3)$ or $(-0.2, -0.2, 2.3)$.

**N-Methylethylenediamine.**—The ring-strain characteristics of chelate rings involving this bidentate are again identical with those of the ethylenediamine rings. The interactions between the methyl group and group A were minimized by the distortion of the angles $\gamma'$ and $\epsilon'$ and of the position of A and by the rotation of A, in the way previously described. For these rings additional positions of A were studied $[(x_A, y_A, z_A) = (0, -0.1, 2.0)$ and $(0, -0.2, 2.0)]$ and it was found that these were more effective than the others in reducing the total energy; both positions led to minimum energy for the ammonia and chloride complexes using Hill's equation but the latter position was necessary to minimize the energies when Bartell's expressions were used.

The studies show that for both complexes and for both Hill's and Bartell's energies the interaction between the methyl group and the ligand A can be mini-

mized when the angle $\gamma'$ is distorted to 114.5°. It is not necessary to distort $\epsilon'$. For this particular ring the interactions of the methyl group are dependent on the value of $Z_1$ rather than on the actual conformation of the ring. Therefore, for each position of the methyl group (defined by $Z_1$) the ring will adjust itself to one of the ethylenediamine conformations with minimized ring-strain energy. Using Hill's equation for the ammine complex the energies for the preferred axial $(Z_1 = -0.4$ to $-0.2$ Å) and equatorial $(Z_1 = +0.4$ to $0.0$ Å)[14] conformations are within the range $1.9 \pm 0.2$ kcal mol$^{-1}$, although there does seem to be a slight energy preference for the equatorial conformation. With Bartell's expressions the equatorial conformation with $Z_1 = 0.0$ to $0.2$ Å is more stable than the symmetrical equatorial conformations by about $0.5$ kcal mol$^{-1}$ and the most favored axial conformations $(Z_1 \simeq -0.4$ Å$)$ by approximately $0.8$ kcal mol$^{-1}$. Using Hill's equation for the chloro complex, the preferred equatorial $(Z_1 = +0.4$ to $+0.6$ Å) and axial $(Z_1 = 0.0$ to $-0.6$ Å) conformations have the energies of $1.9 \pm 0.2$ and $2.1 \pm 0.2$ kcal mol$^{-1}$, respectively.

With Mason and Kreevoy nonbonded interaction energies, the complexes would need to distort an unrealistic amount in order to minimize the large conformational energies. The details of these distortions were not considered in the present study.

### Discussion

In their study of the ethylenediamine chelate ring system, Corey and Bailar[1] specified two rings both of which had the same bond lengths (C–C = 1.54 Å, C–N = 1.47 Å, M–N = 2.00 Å): ring I, $\alpha = 86.2°$, $\beta = 109.5°$, $\angle NCC = 109.5°$, $Z_1 = +0.30$ Å, $Z_2 = -0.30$ Å, $\omega = 48.8°$; ring II, $\alpha = 90°$, $\beta = 104°$, $\angle NCC = 109.5°$, $Z_1 = 0.35$ Å, $Z_2 = -0.35$ Å, $\omega$ unspecified. However, the coordinates of the ring atoms given in the paper for ring I do not yield the stipulated ring parameters, and using the values of $\alpha$, $\beta$, $Z_1$, and $Z_2$ given, the angle $\omega$ is not 48.8° but rather 45°, and for ring II $\omega$ has been calculated to be 55°. Both of these conformations have higher conformational energies than those determined here (see Figure 3).

From the present study it is clear that the chelate ring is very flexible with a wide range of conformations of equivalent energy, including unsymmetrical conformations. This conclusion is strongly supported by an inspection of data on ethylenediamine chelate rings from X-ray structural studies (see Table II). The unsymmetrical distortion of the various bond angles and calculations based on the published atomic parameters show that the rings tend to be unsymmetrical, and with $\omega$ generally in the range 45–55°.

From the study of the propylenediamine complexes it can be concluded that the actual rings for the conformations with the methyl group equatorial and axial are not enantiomeric, that the axial conformation is always unsymmetrical, and that the difference in energy between

(14) When $Z_1 = 0.0$ Å, the "equatorial" conformation has $Z_2$ negative, whereas the "axial" has $Z_2$ positive.

TABLE II

SOME X-RAY STRUCTURAL DATA ON ETHYLENEDIAMINE AND PROPYLENEDIAMINE CHELATE RINGS

| Complex | $\alpha$, deg | $\beta$, deg | $\beta'$,[a] deg | $\omega$, deg | $Z_1$, Å | $Z_2$, Å | Ref |
|---|---|---|---|---|---|---|---|
| trans-[Co(en)₂Cl₂]NO₃ | 85.6 | 106.7 | 112.0 | 48.7 | ±0.48 | ∓0.18 | b |
| trans-[Co(en)₂Br₂]Br·HBr·2H₂O | 86.5 | 109.2 | 108.3 | 45.8 | ±0.35 | ∓0.27 | c |
| d-[Co(en)₃]Br₃·H₂O | 87.0[d] | 108.8 | 104.5 | 50.8 | −0.54 | +0.14 | e |
| trans-[Co((R)-pn)₂Cl₂]Cl·HCl·2H₂O | 88.8 | 103.0 | 101.5 | 63.0 | +0.34 | −0.42 | f |
|  | 87.9 | 107.5 | 106.5 | 46.0 | +0.37 | −0.21 |  |
| l-[Co((R)-pn))₃]Br₃ | 86.5 | 108.0 | 110.0 | 50.2 | +0.31 | −0.39 | g |
| trans-[Cr(en)₂Cl₂]Cl·HCl·2H₂O | 85.2 | 105.8 | 108.3 | 49.1 | +0.22 | −0.40 | h |
| [Cu(en)₂](SCN)₂ | 85.0 | 108.6 | 110.5 | 50.3 | −0.53 | +0.16 | i |
| [Cu(en)₂](NO₃)₂ | 86.2 | 108.5 | 109.1 | 43.6 | +0.39 | −0.19 | j |
| [Cr(en)₃][Ni(CN)₅]·1.5H₂O | 82.6[d] | 109.5 | 108.8 | 52.6 | +0.27 | −0.42 | k |
|  | 82.1[d] | 108.8 | 110.6 | 50.6 | −0.40 | +0.26 |  |

[a] $\beta' = \angle$ MN(2)C(2).  [b] S. Ooi and H. Kuroya, *Bull. Chem. Soc. Japan*, **36**, 1083 (1963).  [c] S. Ooi, Y. Komiyama, Y. Saito, and H. Kuroya, *ibid.*, **32**, 263 (1959).  [d] Average value.  [e] K. Nakatsu, *ibid.*, **35**, 832 (1962).  [f] Y. Saito and H. Iwasaki, *ibid.*, **35**, 1131 (1962).  [g] H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).  [h] S. Ooi, Y. Komiyama, and H. Kuroya, *ibid.*, **33**, 354 (1960).  [i] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **17**, 254 (1964).  [j] Y. Komiyama and E. C. Lingafelter, *Acta Cryst.*, **17**, 1145 (1964).  [k] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

the two types of conformations is between 0 and 3 kcal mol⁻¹. The actual energy difference will depend upon which nonbonded interaction energy expressions are the most realistic. Three means of alleviating van der Waals interactions have been investigated here: distortion of the conformation, distortion of the position of the methyl group relative to the ring, and the distortion of the position of ligand A. The first of these has been found to be the most effective.

When the methyl substituent is on the nitrogen atom, for both its axial and its equatorial orientations limited ranges of symmetrical and unsymmetrical geometries are available for the rings. Within these ranges there are conformations which are enantiomeric with respect to the rings themselves in contrast to the propylenediamine system. The energy differences between the two classes of conformations are even more dependent upon the type of van der Waals energy expression than they are for the previous system. However, the energy difference for the tetraammine complex is certainly less than the value of 4 kcal mol⁻¹ previously calculated[15] using Hill's equation and Corey and Bailar types of conformations. Distortions of the position of A and of the position of the methyl group with respect to the ring are more effective in lessening the nonbonded interactions than the distortion of the ring, again in contrast to the propylenediamine system.

In this study, as in almost all such *a priori* conformational analyses, the main interest is in the geometries of the possible conformations and in the energy *differences* between them, rather than in the actual total conformational energies. It is recognized that there are other terms that contribute to the over-all conformational energy, but it is thought that the majority of these will be canceled when the difference in the energies is determined. Further, the energies calculated are of

course enthalpies. It is not possible at present to estimate the entropy contributions to the total conformational free energy. Experiments are planned in an attempt to determine whether entropy contributes to the energy differences. It could do this by favoring the more flexible conformations. For example, in the propylenediamine complexes, the equatorial conformation has the greatest range of geometries available to it; also, for this conformation, the ligand A (=NH₃) is more free to rotate.

The rotational strength of the d–d transitions of complexes of the type trans-Co((R)-pn)₂Cl₂⁺ is thought to be due almost exclusively to the dissymmetry introduced by the conformations of the chelate rings.[16] The circular dichroism of this complex is almost identical with that of the corresponding (R)-trans-1,2-diaminocyclohexane complex.[16] As a chelate ring involving this bidentate is restricted to the λ conformation, (R)-propylenediamine must have a sizable preference for this conformation in which the methyl group is equatorial. As Hill's equation leads to only small energy differences between axial and equatorial conformations, this suggests that the higher energy nonbonded interactions are more realistic. On the other hand, calculations based on Mason and Kreevoy's expressions would seem to give energy differences that are too large to account for experimental observations.[17] There is a pressing need for some accurate experimental conformational energy differences in order to determine which type of nonbonded interaction energy expression is the most satisfactory.

(15) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).

(16) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

(17) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968); D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **7**, 915 (1968).