Nuclear Quadrupole Resonance Study of Some Hydrogen-Bonded Complexes of Hexamethylenetetramine

JUAN MURGICH,* MAGALY SANTANA R., AND OLGA E. DÍAZ

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 1827, Caracas 1010-A, Venezuela

Received February 16, 1982; revised August 4, 1982

The $^{14}$N NQR spectrum of complexes of hexamethylenetetramine (HMT) with $p$-chlorophenol (1:2) (also the $^{35}$Cl NQR spectrum in this compound), hydroquinone (1:1), and thiourea (1:2) was observed at 77 K. The analysis of the NQR data obtained for the H-bonded and non-H-bonded N atoms in the HMT complexes showed that effects like polarization, exchange, and dispersion are as important as charge transfer in the charge rearrangement produced by weak and moderately strong H bonds. It was also found that the effect of the H bond on the electronic distribution is extended over the entire molecule and that the crystalline electric field also produced additional molecular charge rearrangement.

INTRODUCTION

Considerable attention has been paid to the study of the H bond since its importance in the properties of many compounds of interest in chemistry, physics, and biology. Many techniques have been employed in an attempt to understand the basic features the H bond (1). Molecular orbital (MO) calculations have shown that the H bond produces complex and subtle changes in the molecular charge distribution (2). Experimental results about these changes are scarce as few techniques are able to measure such small charge rearrangements with adequate accuracy (1, 3). Recently the molecular charge distributions of several H-bonded complexes were obtained from X-ray and neutron diffraction data (3). In such a type of calculation one has to deal simultaneously with all the electrons present in the molecules, even those which do not participate directly in the H bond (atomic closed shells, etc.). Consequently the measurement of small charge rearrangements such as those expected in weak H bonds requires a set of data of an accuracy difficult to obtain (3) with the present-day instrumentation. Thus alternative methods have to be found in order to study such charge rearrangements.

As the H bond mainly perturbs lone pair and valence orbitals, one expects that nuclear quadrupole resonance of the atoms involved in such a bond could provide valuable information about the changes produced in the molecular charge distribution by the H bond. From the NQR data one obtains the components of the
electric field gradient (EFG) at the site of a quadrupolar nucleus (4, 5). The EFG describes the asymmetry in the charge distribution around the nuclear site and is very sensitive to any modification in the lone pair and valence bonds distribution (4, 5). As the lone pair provides a major contribution to the EFG, any perturbation such as those expected from weak or moderately strong H bonds involving such atoms produces noticeable changes in its NQR spectrum (4, 5). Marino (6, 7) used 14N NQR spectroscopy in order to study the effects of H bonds on the charge distribution around the N atom in complexes of hexamethylenetetramine (HMT) with some phenols and water. Later Grechiskin and co-workers (8–10) extended that study to a series of complexes of HMT with several inorganic compounds. In all such work, the observed changes in the 14N NQR spectra were interpreted as resulting solely from charge transfer from the N lone pair to the proton donor molecule (6–10). However, several ab-initio MO calculations (2, 11–15) in model compounds such as NH3 and H2O, show that other effects present in the H bond like polarization, dispersion, and exchange are as important as charge transfer in producing charge rearrangements in the molecules participating in H bonds. In view of the MO results it seemed that further work was necessary in order to clarify the relative importance of the different components of the H bond in the charge rearrangement present in the molecules forming these complexes.

The complexes of HMT with substituted phenols and thiourea offer an interesting system for the study of the charge rearrangements produced by the H bond. In such complexes one expects weak or moderately strong H bonds between the N atoms of HMT and the acid protons of the phenols and thiourea (1). Such H bonds do not appreciably modify the molecular geometry (1) so one can make meaningful comparisons between the NQR data obtained for HMT in the complexes with that of pure HMT (4, 5).

Recently the structure of the HMT complexes (16–18) with p-chlorophenol, hydroquinone, and thiourea was determined and it was found that only part of the N atoms of HMT are involved in weak or moderately strong H bonds. The existence of perturbed and unperturbed N atoms in the HMT complexes allows a unique chance to study the extension of the charge rearrangement produced by the H bond around the molecule. Consequently in view of the above results and in order to clarify the relative importance of the different effects produced by the H bond on the molecule, a NQR study of the HMT complexes with p-chlorophenol, hydroquinone, and thiourea was undertaken at 77 K. The results obtained in this work showed that besides charge transfer, other effects like polarization, exchange, etc., make significant contribution to the charge rearrangement produced by the H bonds. It was also found that the whole molecule was affected by the presence of the H bonds in agreement with the predictions of several MO calculations in different model compounds (2, 10–14).

EXPERIMENTAL

The HMT–2 p-chlorophenol complex was obtained from a mixture of aqueous solutions containing stoichiometric amounts of p-chlorophenol and HMT. The resulting mixture was heated in a water bath for 30 minutes and let stand for several weeks. Transparent needles were collected and recrystallized from a 50/50 water–
ethanol mixture (mp 97 to 98°C). The HMT–hydroquinone complex was obtained from the mixture of hot solutions of stoichiometric amounts of the components in ethanol. A precipitate formed by fine needles was obtained immediately after mixing (mp 200 to 201°C, reported 201 to 202°C) (17). The HMT–2 thiourea complex was prepared as in Ref. (18), (mp 161 to 162°C). All the components and solvents were carefully purified either by distillation or recrystallization from reagent-grade chemicals. The $^{14}$N spectra were observed at 77 K in a cw spectrometer equipped with a Robinson oscillator–detector similar to that of Ref. (19). Samples of around 20 cm$^3$ were used in the study of the $^{14}$N NQR spectrum of HMT complexes. The $^{35}$Cl NQR spectrum of the HMT–2 p-chlorophenol complex was obtained at room temperature with a superregenerative spectrometer similar to that used in Ref. (20).

### Table 1

<table>
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<tr>
<th></th>
<th>Unperturbed N</th>
<th>Perturbed N</th>
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<td>$e \eta Q/h$</td>
<td>$e \eta Q/h$</td>
<td>$4 \frac{1}{3} (\alpha_1 - \alpha_2)$</td>
<td>$4 \frac{1}{3} (\alpha_2 - \alpha_1)$</td>
<td>$</td>
<td>\sigma_1 - \sigma_2</td>
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<td>HMT$^a$</td>
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$^a$ In case of multiple N sites all possible combinations were considered.


$^c$ Refs. (6) and (7).
RESULTS

Since $^{14}\text{N}$ has a nuclear spin equal to 1, the $^{14}\text{N}$ NQR spectrum generally consists of three lines (4, 5). If $q_{xx}$, $q_{yy}$, and $q_{zz} = q$ are the three diagonal components of the EFG in its principal axis system defined so that $|q_{xx}|=|q_{yy}|=|q_{zz}|$, the frequencies of the lines are then (4, 5)

$$v^+ = \left(\frac{eqQ}{4\hbar}\right)(3 \pm \eta),\quad [1]$$

$$v^0 = v^+ - v^-,\quad [2]$$

where $Q$ is the nuclear electric quadrupole moment and $\eta$, the asymmetry parameter, is defined as $\eta = (q_{xx} - q_{yy})/q_{zz}$. In Tables 1 and 2 are shown the $^{14}\text{N}$ and $^{35}\text{Cl}$ NQR data obtained for several complexes of HMT. The $^{14}\text{N}$ data corresponding to HMT in these complexes is also shown in Fig. 1. From the latter figure one sees that the $^{14}\text{N}$ lines are distributed in two sets; one located at lower frequencies than pure HMT ($\sim$ −200 kHz) and the other located at higher frequencies ($\sim$ +100 kHz). Marino (6, 7) assigned the high-frequency set to the unperturbed N atoms while the low-frequency set was assigned to the perturbed atoms of HMT. As seen from Fig. 1, the same distribution was observed in the complexes studied in this work so it is reasonable to assume the same assignment is valid for these HMT complexes.

In the hydroquinone complex, three weak $^{14}\text{N}$ lines were found in the frequency range assigned to unperturbed N atoms. A Zeeman study showed that the line located at 3480 kHz behaved as belonging to a N atom with $\eta = 0$. The room-

<table>
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<tr>
<th>$\nu^+$ (kHz)</th>
<th>$\nu^-$ (kHz)</th>
<th>$\nu$Q/h (kHz)</th>
<th>$\eta$</th>
<th>$\nu - \bar{\delta}_{\text{NH}}$</th>
<th>$\bar{\delta}<em>{\text{NH}} - \sigma</em>{\text{NC}}$</th>
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<td>0.265</td>
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<tr>
<td>$^{35}\text{Cl}$</td>
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<tr>
<td>$p$–Chlorophenol$^b$</td>
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<td>3430.3</td>
<td>0.096 ± 0.001</td>
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<td>34077</td>
<td>0.071 ± 0.002</td>
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<td>HMT–2 $p$–chlorophenol</td>
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<td>3380.6 ± 5</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>33278 ± 5</td>
<td></td>
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$^a$ Also are shown the $^{35}\text{Cl}$ NQR frequencies for $p$–chlorophenol and its HMT complex.

$^b$ Reference (22).

temperature crystal structure of the hydroquinone complex (17) shows that the asymmetric unit contains three types of N atoms with only two of these atoms involved in H bonds of medium strength (17). The intensity and multiplicity of the $^{14}$N spectrum of the hydroquinone complex shows that there are the same number of perturbed and unperturbed N atoms in the asymmetric unit at 77 K as at room temperature (17).

The p-chlorophenol complex gave an eight-line $^{14}$N spectrum and a Zeeman study showed that all the lines belonged to N atoms with finite values of $\eta$. Two weak $^{35}$Cl NQR lines of approximately the same intensity were found at room temperature for this complex. The number and intensity of the N and Cl lines plus the reported stoichiometry of the p-chlorophenol complex indicate the existence of an asymmetric unit containing two inequivalent Cl sites and four inequivalent N sites. The above conclusion is valid only if no phase transition that changes the number of inequivalent sites in the crystal occurs between 77 K and room temperature.

In the thiourea complex a spectrum formed by eight $^{14}$N lines was observed at 77 K. From Fig. 1 one sees that the upper quartet corresponds to perturbed and unperturbed N sites in HMT. The lower quartet, not shown in Fig. 1, corresponds to amido N atoms as their frequencies are close to those of pure thiourea (21). A Zeeman study showed that all the lines corresponded to N atoms with finite $\eta$ values indicating that the set of perturbed (unperturbed) N atoms of HMT are equivalent while those N atoms corresponding to the thiourea molecule are all inequivalent. The above results show that the structure of the complex at 77 K has the same number of equivalent (inequivalent) N sites as at room temperature (10).

**DISCUSSION**

In the interpretation of the NQR data obtained in the HMT complex it is convenient to consider the energies involved in the H-bond formation and their effects on the molecular charge distribution. The total intermolecular interaction energy of weak and moderately strong H bonds can be partitioned in the following components (12, 14) (a) electrostatic (Coulomb) energy, (b) polarization energy, (c) charge transfer energy, (d) exchange (repulsive) energy, and (e) dispersion energy. The electrostatic contribution corresponds to the variation in the energy that should result if the free constituent molecules were brought together into the positions corresponding to the H-bonded complex, without any electron exchange or redistribution. The polarization contribution corresponds to the energy gained on deforming the charge distribution of the participating molecules in the previous state.
to correspond more closely to the final charge distribution but without any intermolecular charge transfer. The charge transfer contribution represents the energy gained in also allowing electron transfer between the molecules forming the complex. The dispersion contribution corresponds to the gain in energy originating in the correlation of the electron motion of the components (London dispersion forces). The repulsive term corresponds to the exchange energy that is directly related to the Pauli exclusion principle and avoids the collapse of the molecules forming the complex. Several ab-initio MO calculations of water dimers (15) and other weakly or moderately strong H-bonded complexes showed that the polarization, exchange, charge transfer, and dispersion terms approximately cancel each other at the complex equilibrium geometry and that the changes in electrostatic energy follow the same tendency as the total H-bond energy (12, 14). The above separation scheme is only valid in weak and moderately strong H-bonded complexes where the geometry of the molecules of the components is not changed by the interaction. The HMT molecule seems to fulfill this requirement, as the geometries of all molecules involved in complexes studied in this work do not change appreciably upon complex formation (16, 17) and all the N-H distances correspond to H bonds of intermediate strength or to values equal or longer than the sum of their van der Waals radii (22).

Further information about the role and weights of the different components of the energy separation scheme on the charge redistribution upon H-bond formation could be obtained from ab-initio MO calculations (2, 11-15). As this type of work is prohibitively expensive for the HMT complexes studied in this work, one has to use calculations made for smaller molecules as indicative of the changes produced by the H bond. Dreyfus and Pullman (2) studied the formation of formamide dimers and found that the polarization and charge transfer contribute appreciably to stabilize the complex. The amount of actual charge transfer was found in the weak H-bonded complexes to be very small (2). However, it was found that a significant reorganization inside each molecule participating in the H bond occurred as a result of the formation of the complex. The exchange and polarization components contribute to the electron displacement, the first component being, however, confined to the O-H-N part of the dimer. The MO studies of the changes produced by the H bond in the molecular charge distribution have been confined, in general, to the supermolecular approach (2, 11-15). Few attempts have been made to study the additional changes produced by the presence, in the crystal, of charges outside the complex unit. As NQR is a solid-state technique, such additional contribution to the EFG could be of importance in the analysis of the data obtained in the HMT complexes (23, 24). Amlsf et al. (25) studied several solid hydrates and found that significant changes in the EFG of the H nucleus are caused by the polarization of the bonds and by the change in geometry produced by the electric field arising from the external charges. It is likely that a similar effect could be present in the HMT complexes, however, the rigid structure of that molecule would tend to reduce the contribution coming from deformation (16-18).

From the point of view of NQR, the charges outside the complex unit produce two types of contributions to the total EFG: a direct one that is added to the gradient seen by the quadrupolar nuclei (23), and an indirect one that arises from (a) the
induced polarization of the orbitals (electronic polarization) and (b) the changes in molecular geometry (atomic polarization) produced by the external field. The direct contribution to the EFG has been found to be very small in the molecular crystals where such calculations have been made (6) so it will be neglected in this work. The indirect contribution is much more difficult to estimate as it requires detailed knowledge of the polarization of the different orbitals of the components of the H-bonded complex and an accurate determination of any change in the molecular geometry. However, some qualitative arguments could be advanced as it is known that the atomic polarization (a.p.) in the majority of the organic molecules is much smaller than the electronic polarization (e.p.) (a.p. ~ 10% e.p.) (26). In view of the constancy of the HMT bond length and angles (16-18) one could reasonably assume that the most important part of the polarization produced by the crystalline field in the HMT complexes is the electronic polarization as the geometry of the HMT molecules is practically unchanged (17).

**Townes and Dailey Analysis**

The Townes and Dailey theory relates the NQR data with the population of the different N (Cl) orbitals (4, 5). From the crystal structure of the HMT complexes (16, 18) one sees that the N atoms have an sp³ hybridization geometry with three N-C σ bonds with population σ_{NC} and a nonbonding orbital (lone pair) with population \( l \). Assuming that the principal \( z \) axis of the EFG is directed (4, 5) along the nonbonding orbital and that one of the σ bonds has a different population from that of the other two bonds (\( σ_1 ≠ σ_2 \)), it can be shown that (4, 5)

\[
α = (e^2qQ/e^2q_0Q) = (3/4)(1 - \bar{u}),
\]

\[
α\eta = |σ_1 - σ_2|,
\]

where \( e^2qQ/ℏ \) is the quadrupole coupling constant per unbalanced 2p electron (=10 MHz) (4, 5) and \( \bar{σ}_{NC} = (1/3)σ_1 + (2/3)σ_2 \). In Table 1 are shown all possible values of \( Δl = Δσ \) and \( |σ_1 - σ_2| \) for both perturbed and unperturbed N atoms in the HMT complexes.

For the amino group of thiourea, and assuming equal N-H bonds, one has (4, 5)

\[
α(1 - η/3) = (π - σ_{NH}),
\]

\[
α = (3/2)(σ_{NH} - σ_{NC})(1 - cot^2γ),
\]

where \( π \) is the population of the N nonbonding orbital located perpendicular to the molecular plane and \( σ_{NH}(σ_{NC}) \) are the population of the N-H (N-C) σ orbital. The angle \( 2γ \) corresponds to the HNH bond angle and was obtained from the available crystal structures (16-18). The results for thiourea are shown in Table 2.

As the \(^{35}\)Cl has nuclear spin equal to 3/2, only one frequency per site is found in polycrystalline samples (4, 5), with \( ν = (e^2qQ/2ℏ)(1 + η^2/3)^{1/2} \). For organic compounds such as \( p \)-chlorophenol \( η < 0.1 \) so one may, in first order, assume that the NQR frequency is determined by the component of the EFG along the Cl-C axis (4, 5). The results for \(^{35}\)Cl are shown in Table 2.
From Table 1, one sees that the values of $\Delta l - \Delta \sigma$ found for unperturbed N atoms in the HMT complexes are smaller in magnitude and of the opposite sign than the values found for the perturbed N atoms. One sees also from Fig. 1 that $\Delta l - \Delta \sigma$ is negative for the perturbed N atoms indicating that $|\Delta l| > |\Delta \sigma|$ and that $\Delta l < 0$. Such value of $\Delta l$ may be interpreted as the result of charge transfer from the lone pair to the proton donor molecule (5, 10). In order to test this interpretation one may use a model developed for the analysis of the NQR data of coordinated N atoms (27). In that model it is assumed that the loss of the N lone pair population induces an increase in the N–C $\sigma$ and $\pi$ population and one has then that $\tilde{\sigma} = \tilde{\sigma}_0 + A (2 - l)$, where $\tilde{\sigma}_0$ ($\bar{\sigma}$) is the average population of the N–C $\sigma$ bond in pure (complexed) HMT and $A$ is a constant. The substitution of $\tilde{\sigma}$ in Eqs. [2] and [3] gives a relation (27) between $\sigma$ and $\eta$ of the type $1/\alpha = C + D\eta$, where $C$ and $D$ are also constants. A linear correlation between the values of $1/\alpha$ and $\eta$ in the HMT complexes would indicate that the charge transfer--induction model is able to properly describe the changes occurring upon H bonding. A plot of $1/\alpha$ and $\eta$ values obtained for the perturbed N atoms of the HMT complexes fails, however, to give any correlation between these two quantities. The absence of correlation between $1/\alpha$ and $\eta$ shows that other terms besides charge transfer and induction are important in the charge rearrangements found in these complexes. From the above result it is clear that $\Delta l$ reflects not only the actual charge transfer as assumed before (6, 11) but also other effects like polarization, etc., that are present in the H bond. This last result is in accord with several MO calculations in model compounds in which it was found that terms like polarization, etc., also contribute appreciably (2, 10–15) to the molecular charge rearrangements produced by the H bonds.

The Crystalline Contribution

As pointed out above, the NQR results include the effect of the crystalline electric field on the charge distribution of the HMT molecule. In a crystal, the internal electric field reflects the lattice symmetry and may produce different effects depending on the site occupied by the resonant atom in the unit cell (23). The hydroquinone complex offers an opportunity for the study of such an effect, as the unperturbed N atoms of the HMT molecule (which are chemically equivalent by symmetry) occupy different general positions in the crystal (17). From Eq. [4] one expects to find a finite value of $\eta$ for both unperturbed atoms as they are linked to different types of N atoms through the $-\text{CH}_2-$ groups ($\sigma_1 \neq \sigma_2$). From Table 1 it is seen that this is not the case as both unperturbed N atoms differ in their $\eta$ values ($\eta = 0.017$ and $\eta = 0.000$) and in the $e^2 q Q/h$ values (4640 and 4621 kHz). These differences show that in certain cases the crystalline field is able to change the values of $\tilde{\sigma}_{NC} (\sigma_1, \sigma_2)$ in such a way that the expected inductive contribution is suppressed ($\eta = 0$, or $|\sigma_1 - \sigma_2| = 0$).

From Table 1 it is seen that the values of $|\sigma_1 - \sigma_2|$ for the HMT complexes cover a rather wide range of values. In view of the different structures of the HMT complexes (16–18) and the contribution of the crystalline field to the $\sigma_{NC}$ values found in the hydroquinone complex it is reasonable to expect similar contributions in the
other complexes besides that of hydroquinone. Consequently one may expect that the values of $|\sigma_1 - \sigma_2|$ include sizable contributions from the crystalline field in complexes with weak or moderately strong H bonds.

**Perturbed and Unperturbed Nitrogens**

It is interesting to compare the average frequency shift of perturbed ($\Delta\nu_p$) and unperturbed ($\Delta\nu_{up}$) N atoms found in the HMT complexes. From such a comparison one expects to obtain information about the extension of the perturbing effect of the H bond on the molecular charge distribution. From Fig. 1 it is found that $\Delta\nu_{up}$ has values between 20 to 80% of those observed for $\Delta\nu_p$. This fact shows that the H bonds also modify the charge distributions around the unperturbed N atoms sometimes in a quite noticeable way. These changes are produced through long-range effects like polarization, etc., with additional contributions from the crystalline field. As pointed out above it is difficult to estimate the crystalline contribution, but one sees from Table 1 that all the $\Delta\nu_{up}$ are positive even if the unperturbed N atoms occupy quite different positions in the unit cell. One may conclude from this fact that the main component responsible for $\Delta\nu_{up}$ is related to the existence of H bonds and that the crystalline field produces only a perturbative effect. In view of the magnitude of the $\Delta\nu_{up}$ it seems that the H bond produces charge rearrangements that extend over the whole molecules as predicted by the MO calculations (2, 3).

**Thiourea**

The $^{14}$N NQR data obtained for thiourea in the HMT complex provided information about the proton donor molecule participating in an H bond. Unfortunately thiourea also forms a complicated network of H bonds in its pure state (28). Consequently one may only obtain information about changes in that network and not absolute differences as in the HMT case where no H bonds are present in the crystal of the pure compound. The crystal structure of the thiourea complex obtained at room temperature (17) shows that only three of the four amino H atoms are involved in such bonds, as structural reasons prevent close contact of one of them with neighboring molecules. In Eqs. [5] and [6] it was assumed that the N-H bonds were equivalent. If the differences are not marked one may still use these equations for obtaining averaged values of $\sigma_{NH}$. Support for such procedure may be obtained from the single-crystal work of Smith and Cotts in pure thiourea (27). These authors found that inequivalent N--H bonds produced only slight changes in the EFG so one may expect that in HMT-2-thiourea complex a similar situation exists as the H-bond network is not markedly different from that found in pure thiourea (22). From Table 2 one sees that the thiourea molecule shows an increase in the values of $\bar{\sigma}_{NH} - \sigma_{NC}$ and a decrease in the values of $\pi - \bar{\sigma}_{NH}$ upon complex formation. Also it is seen that the changes in $\pi - \sigma_{NC}$ are smaller than those found in $\bar{\sigma}_{NH} - \sigma_{NC}$ values. When the HMT complex is formed a rearrangement in the H-bond network around the thiourea molecule takes place. Several N--H . . . S--H bonds are replaced by stronger N--H . . . N bonds (22). One expects that such changes would increase the values of $\bar{\sigma}_{NH}$ as predicated by MO calculations in several model compounds (2, 12-15). From Table 2 one sees that this seems to be the case for
thiourea as the changes in the population of the amino N atoms in passing from pure thiourea to the HMT complex may be interpreted as resulting from an increase in the values of $\bar{\sigma}_{\text{NH}}$. The difference in the behavior of $\pi - \bar{\sigma}_{\text{NH}}$ and $\bar{\sigma}_{\text{NH}} - \sigma_{\text{NC}}$ upon complexation may be interpreted as resulting from a larger variation in the $\pi$ orbital population than in the N-C $\sigma$ orbital originated in the higher polarizability of the N $\pi$ orbital (29). A similar behavior for the changes in the $\pi$ and $\sigma_{\text{NC}}$ values was found in a series of complexes of urea with several acids (29).

$p$-Chlorophenol

The number of inequivalent Cl and N sites found in the HMT-$p$-chlorophenol complex indicates a complicated asymmetric unit and H-bond network. The observed decrease in the $^{35}\text{Cl}$ NQR frequency shows that the Cl-C bond becomes slightly more ionic when the complex with HMT is formed (4, 5). The average frequency shift found is slightly larger than the values attributed to the crystalline field contribution (23) (~500 kHz) thus indicating a rearrangement in the charge distribution at the Cl atom in the $p$-chlorophenol molecule in its HMT complex.

Dynamical Factor

The EFG measured by NQR is an average over the molecular librational motion (4, 5). So when one compares the EFG measured for the same molecule in different structures one has to take into account the fact that the average may be quite different in each case (23). Unfortunately a calculation of the averaging process in the HMT complexes is beyond the capability of the present-day solid-state theory (4, 5, 23). However, qualitative information could be obtained from the comparison of the temperature dependence of the NQR spectrum of pure HMT and in some of its complexes. Marino (6, 7) and Grechiskin and co-workers (8, 10) found that the temperature dependence of the $^{14}\text{N}$ NQR spectrum of pure HMT and of some of its complexes was quite similar. From these results one could reasonably assume that the thermal averaging in both cases is not markedly different. In view of these results one may conclude that the frequency shifts observed upon complex formation in HMT could be attributed mainly to the present of H bonds and crystalline field effects (23).

SUMMARY

The comparison of the $^{14}\text{N}$ NQR data of pure HMT and that corresponding to the perturbed and unperturbed N atoms of the same molecule in several of its complexes showed that the presence of H bonds produced complicated changes over the whole molecular charge distribution. It was also found that (a) the changes in the $^{14}\text{N}$ NQR data cannot be attributed only to charge transfer from the N lone pair to the OH group, and (b) other factors also present in the H bond, like polarization, exchange, etc., are important in the charge rearrangements produced by the complex formation. Additionally it was found that the crystalline field perturbs the charge distribution of HMT in the solid state and in one case (hydroquinone) overcomes the expected inductive effect produced by the existence of perturbed and
unperturbed N atoms. The NQR results obtained in some proton donor molecules like thiourea and p-chlorophenol show that there are measurable changes in their charge distribution as a result of changes in their HB network upon complex formation.

REFERENCES