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An Investigation of Molecular Reorientation in Crystalline Pyrazine by Pulse NMR and The Atom–Atom Approximation for Intermolecular Forces†

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Proton NMR relaxation times (T_1 at 9.2 MHz and 18.5 MHz, and T_1 at 18.5 MHz) have been measured for crystalline pyrazine over the temperature range 293 K to the melting point at 327 K. No evidence of a discontinuity in these data is evident at either 29°C or 35°C, where previous workers have found evidence of a phase transition using infrared, Raman, ^{14}N NQR, calorimetric and other techniques. This result was valid for both unpurified samples and for samples obtained as the result of fractional sublimation. With the assistance of potential energy calculations using the atom-atom approximation for intermolecular forces, the nature of the motional process responsible for the spin-lattice relaxation has been proposed to be an in-plane flip by 180 degrees; this proposal appears to be consistent with all experimental information available for the low-temperature phase stable below 29°C. In addition, the nature of the first phase transition at 29°C has been similarly investigated; it is suggested that this involves an in-plane rotation by 90 degrees of just one of the two molecules in the unit cell. Again, this suggestion seems capable of rationalising all available information concerning this transition, although it is possibly not unique in this regard.

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† Taken in part from the M.Sc. thesis of W. E. Sanford, University of Guelph, 1975.

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I INTRODUCTION

Considerable work has been done on the physical properties of crystalline pyrazine. An X-ray diffraction study of the crystal structure at 20°C (293 K) was published by Wheatley some time ago.[1] More recently,[2,3] infrared and Raman spectra of crystalline pyrazine have been obtained at different temperatures; the results obtained[2,3] suggested that a phase transition might occur near room temperature, and a search by differential scanning calorimetry[3] revealed a thermal anomaly at 29°C (320 K), with a measured enthalpy of transition $\Delta H_t = 263(\pm 10)$ cal mol^{-1}. The structural information obtained from the infrared and Raman spectra[2,3] below this transition was consistent with the x-ray structure,[1] but at higher temperatures it seemed necessary to postulate the existence of a different structure. More recently, a study[4] of the temperature of the ^{14}N quadrupole coupling constants in pyrazine indicated the existence of *two* transitions; the first at 27°C (300 K) involved a splitting of the NQR lines, and probably coincides with the thermodynamic transition[3] at 302 K to within experimental uncertainty. However, the NQR data displayed a second discontinuity[4] at 35°C (308 K), which was not apparent in the IR, Raman, or calorimetric results.

Additional useful information on the nature of the phase transition at 29°C was obtained[2] by observing the transition with a polarising microscope; it was concluded[2] that the crystal axes have the same orientation in the two crystal forms recognised in this earlier work.[2] The evidence from infrared spectroscopy[2] demonstrated the transition to be reversible and appreciably free from hysteresis; when obtained using polarised light and well-oriented samples,[2] the orientation was fully preserved through the transition point, even if the sample was taken back and forth several times through the transition. Moreover, the directions of extinction were found[2] to coincide for the crystalline forms stable above and below the transition temperature.

Finally, the coherent inelastic scattering of neutrons by perdeuterated pyrazine crystal at room temperature has been used[5] to determine the lattice vibrations in the Brillouin zone. In addition, a theoretical model of the small-amplitude lattice dynamics was used[5] in an attempt to account for the observed phonon spectrum in terms of non-bonded intermolecular interactions; the latter were approximated[5] by the atom-atom model.

The purpose of the present work was to obtain proton spin-lattice relaxation times over the appropriate temperature range, using various techniques of pulse NMR, to determine whether such methods could yield additional useful information. In addition, the atom-atom approximation to intermolecular forces in crystals has presently been applied to the reorientation motion of the pyrazine molecule in its crystal lattice; such application has been described previously for planar aromatic hydrocarbons[6] and heterocyclic molecules.[7,8]

II EXPERIMENTAL

The pyrazine sample, purchased from Aldrich Chemical Co., was stated to be of better than 99% purity. Most of the results reported here were obtained using the sample as supplied, without further purification. However, a few measurements were made using a sample obtained as the result of a fractional sublimation procedure; no differences were detectable between the T_1 value obtained for the two samples. The measurements of the spin-lattice relaxation time T_1 were performed using the 90° pulse saturation technique,[9] which offered the most convenient method for the rather long relaxation times observed. These measurements were conducted at 18.5 MHz using the equipment constructed at Guelph and described previously;[8] values of T_1 at 9.2 MHz were obtained on a Bruker SXP variable frequency spectrometer. The measurements of T_{1D} were obtained at 18.5 MHz using the Guelph equipment, using the pulse sequence suggested by Jeener and Broekhart.[10]

The calculations of potential energy for a rigid test molecule moving about a fixed lattice site in the pyrazine crystal were first performed essentially as described previously[8] for furan and for thiophene. The available crystal structure of pyrazine[1] refers to a temperature of 20°C (293 K), well below the phase transitions;[3,4] the structure appears to be perfectly ordered. However, the carbon-hydrogen bond-length[1] of 0.105 nm is appreciably shorter than the usual value for planar aromatic compounds (0.108 nm), and is also smaller than the value of 0.109 nm determined[11] by electron diffraction for gas-phase pyrazine. Accordingly, the hydrogen atom coordinates used in the present computations were generated to correspond to a carbon-hydrogen bond-length of 0.108 nm; however, the angles made by the carbon-hydrogen bonds with the carbon-nitrogen skeleton were assumed to be those determined[1] by x-ray diffraction. For such a simple model, which assumes that all atoms, including the nitrogen atoms, are spherically symmetrical, the results obtained were not wholly satisfactory, though similar to those obtained previously by Gavezzotti and Simonetta.[12]

A more successful approach was based upon that adopted by Mason and Rae[16] for the case of *s*-triazine, and by Fyfe and Harold-Smith[7] to account for the behaviour of crystalline hexamethylenetetramine; in this model,[7] each nitrogen atom is replaced by an isoelectronic carbon-hydrogen group, thus simulating the directional properties of the nitrogen atom with its lone pair of electrons. The "best bond length" for such a conceptual carbon-hydrogen group was determined[7] to be about 0.07 nm, and this value was used in the present work. The parameters used for the potential functions for carbon and hydrogen atoms were those due to Williams[13] determined previously[6] to account most satisfactorily for the behaviour of aromatic hydrocarbons.

The electrostatic contributions in this model were, however, subject to some uncertainty. This is because the lone-pair is a small lobe of negative charge, and not an essentially neutral carbon-hydrogen bond, as assumed previously.[7] While the total electrical charge on the nitrogen atom, and thus on its replacement carbon-hydrogen group, may be estimated by molecular orbital calculations,[14] the splitting of this total charge into (assumed) point-charges on the "conceptual" carbon and hydrogen atoms, presents a non-trivial problem. This was solved in the present work following previous work by Reynolds,[5] by using an estimate of 2.2 Debyes for the local dipole moment of the lone-pair electrons on the nitrogen atom in pyridine, obtained[15] by NQR measurements of the electric field gradient at the nitrogen atom. This experimental value is in reasonable agreement with a theoretical estimate, due to Coulson, of 1.7 Debyes, used previously by Mason and Rae[16] for the case of *s*-triazine. Together with the "best bond length" of 0.07 nm for the "conceptual" carbon-hydrogen group replacing the nitrogen atom with its lone-pair, this value for the dipole moment permitted the following assignment of electric charges, (expressed in terms of fractions of the electronic charge):

Carbon atoms, +0.0745
Hydrogen atoms, 0.0000

$$\left.\begin{array}{l}\text{“Conceptual” carbon atoms, } +0.5755\\ \text{“Conceptual” hydrogen atoms, } -0.7245\end{array}\right\}\begin{array}{l}\text{Replacement for nitrogen}\\ \text{atom plus lone-pair}\end{array}$$

These unusually large charges, assigned to the atoms within each carbon-hydrogen group assumed to replace a nitrogen atom, are a quantitative reflection of the fact that a lone-pair on a nitrogen atom represents a negatively-charged lobe; approximation of this feature by a point centre of interaction, as is done here, requires a large negative charge to be assigned, if the model is to be at all realistic.

Shielding of the electrostatic interaction between two atoms by a third atom situated between them is a three-body effect of considerable complexity. It would certainly be wrong to approximate this effect through the use of the bulk dielectric constant. In the present work, this effect was ignored (dielectric constant set to unity); while the electrostatic contribution to the total lattice energy was unusually large, as found previously,[5] this is dominated by close interactions between negatively charged lone pairs with positively charged carbon atoms, with *no* intervening third atom, (see packing diagram given by Wheatley[1]). Thus, this particular approximation should not be too serious in this case.

III RESULTS

The NMR relaxation times are shown plotted as log T_1 (or log T_{1D}) vs. the reciprocal of absolute temperature in Figure 1. At both radio frequencies ω_0 employed, the T_1 values decrease monotonically with increasing temperature without reaching a minimum; further, at a fixed temperature, T_1 varies at ω_0^2. Assuming that the relaxation processes responsible for the observed T_1 behaviour can be attributed entirely to fluctuations of the ^{1}H nuclear dipole interactions mediated by molecular reorientations, these temperature and frequency dependences of T_1 indicate that the molecular motions are slow, i.e. $\omega_0 \tau_c \gg 1$, where τ_c is the correlation time for the motion. The activation energy for the motion, derived from the slopes of the T_1 plots, is 14–15 k cals mol^{-1}; no evidence of a phase transition is evident in Figure 1.

The T_{1D} data display a minimum value of about 0.4 msec at about 33°C; this behaviour may be interpreted as indicating $\tau_c \sim 1/\gamma H_L$, where H_L is the local proton dipolar field. The T_{1D} data are generally consistent with the activation energy derived from the T_1 results. No evidence was found for the onset of an additional, slower motion as the temperature was raised near the melting point; such a motion has been observed previously[8] for benzene, furan and thiophene for example, and tentatively identified as self-diffusion.

The potential-energy calculations were performed for motion of an (assumed) rigid pyrazine molecule at its fixed lattice site, about each of three mutually perpendicular axes; the labelling of these axes was chosen to correspond to that used in previous work. Thus, the N-N axis is the OZ axis, the in-plane axis perpendicular to the N-N axis is the OX axis, and the C_2 axis perpendicular to the molecular plane is the OY axis. The potential energy profiles for rotation of the test molecule about each of these molecular axes are shown in Figure 2–4. Those corresponding to rotations about the OX and OZ axis are similar, requiring impossibly large activation energies for rotation. However, both are characterized by very broad minima at the crystallographic positions; thus, expenditure of the experimentally determined activation energy is sufficient to provide a considerable angular displacement about either of the OX or OZ axes.

The in-plane rotation about the OY molecular axis characterized by several features; the crystallographic position is apparently a double minimum, at -11 to -12 k cals mol^{-1}, with a small energy barrier separating

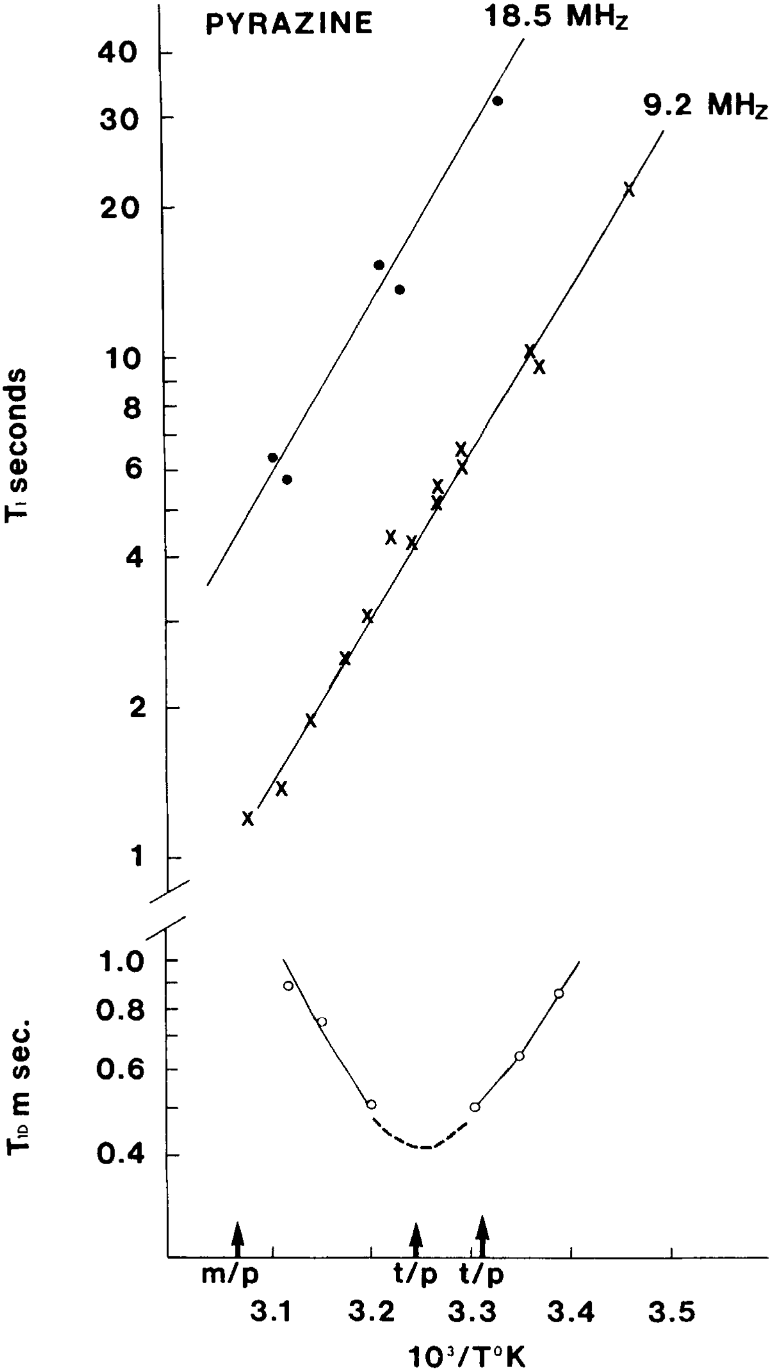

FIGURE 1 The variation of T_1 (upper two curves) and T_{1D} (lowest curve) with temperature for polycrystalline pyrazine. The arrows indicate the two solid-solid phase transitions observed for pyrazine at 29°C and 35°C, as well as the melting point at 54°C.

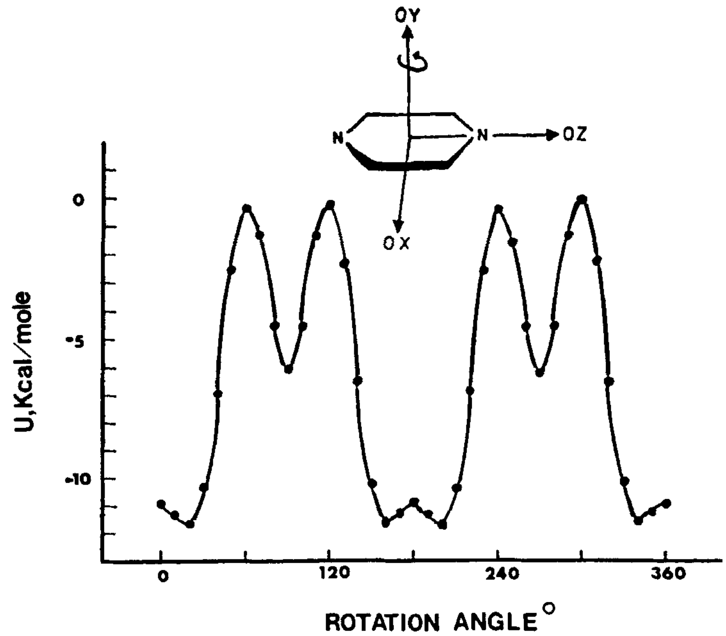

FIGURE 2 Potential energy profile for in-plane rotation of a pyrazine molecule in its low-temperature lattice.

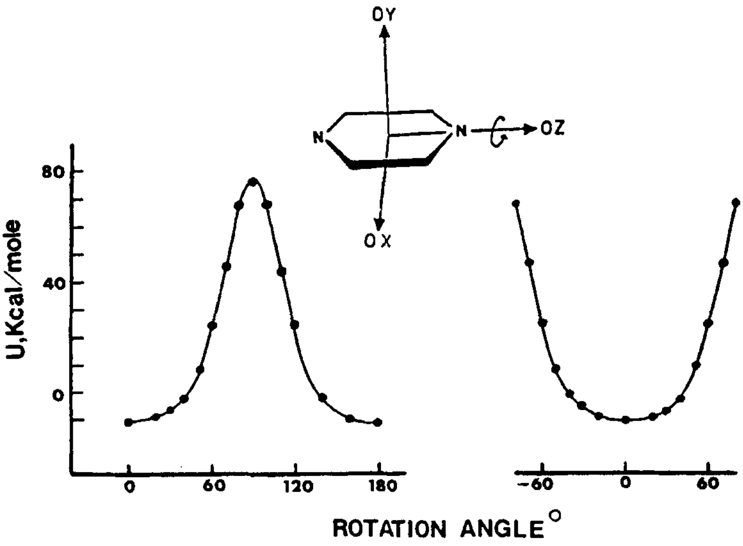

FIGURE 3 Potential energy profile for rotation of a pyrazine molecule about the N-N axis, in the low-temperature lattice.

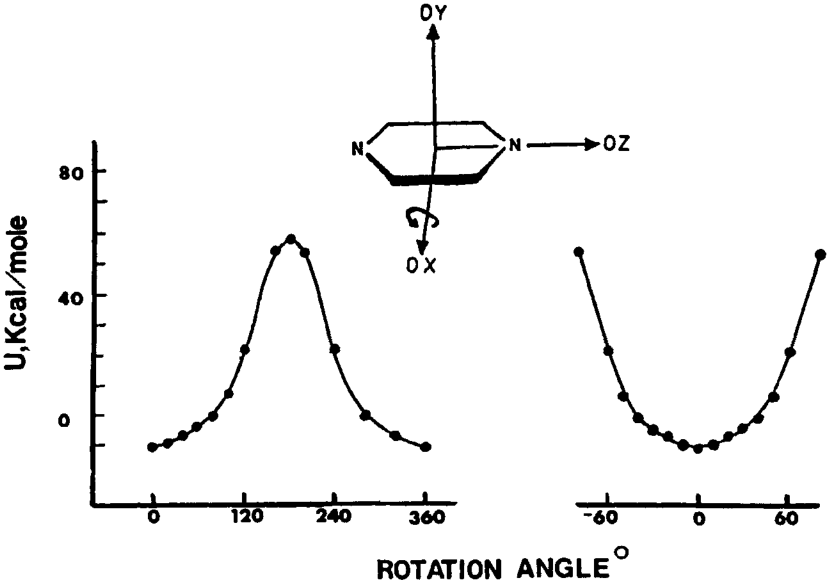

FIGURE 4 Potential energy profile for rotation of a pyrazine molecule about an axis within the molecular plane and perpendicular to the N-N axis, in the low-temperature lattice.

two minima situated at ±20° from the crystallographic position. This feature could easily be an artefact of the many approximations involved in the model, or at least the true size of the barrier could be much lower than that estimated here. A more clearly defined result is the existence of a sub-minimum at 90° from the crystallographic orientation, as was found previously;[12] the population in this sub-minimum, at room temperature, would be far too small to be detected by x-ray diffraction.

The energy barrier for in-plane rotation about the OY axis is seen from Figure 2 to be about 23 k cals mol^{-1}. (As pointed out recently by Busing,[17] previous work of this type[6–8,12] has misinterpreted computed profiles like Figures 2-5; the quantity to be compared with the observed activation energy is *twice* the barrier height. In the present case, as previously, computed barriers may be obtained in closer agreement with experiment through use of an alternative parametrisation of the potential functions.[18] The present work, which was completed before this error of interpretation was drawn to our attention, used a parametrisation[13] of the potential functions characterised by a relatively large repulsive contribution; use of an alternative set of parameters corresponding to a "softer" repulsive interaction, also due to Williams,[19] would yield much better quantitative agreement between calculation and experiment[18]).

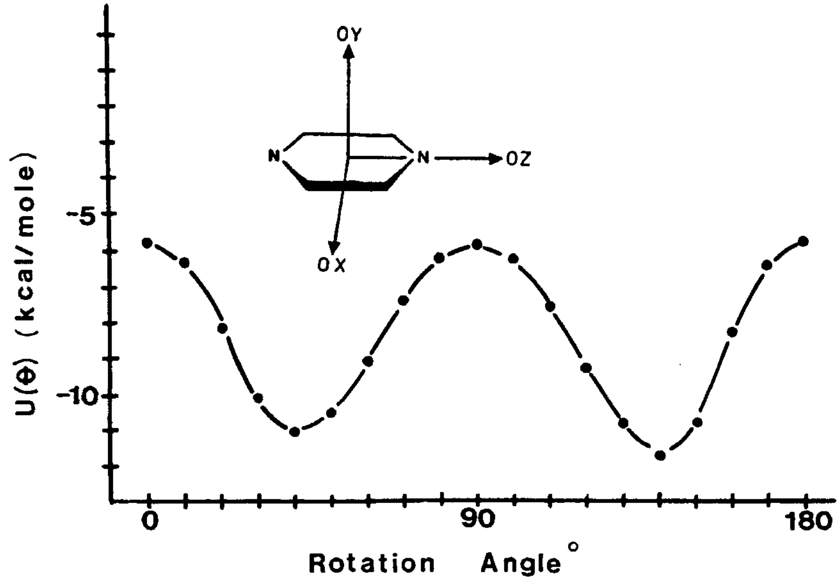

FIGURE 5 Potential energy profile for in-plane rotation of a pyrazine molecule in a model lattice generated from the low-temperature lattice by an in-plane rotation of all molecules by 90 degrees.

Additional computations of this type were carried out; however, it is more convenient to describe the motivation for, and results of, these calculations after discussion of the results described thus far.

IV DISCUSSION

(a) Low temperature phase

The T_1 and T_{1D} data (Figure 1) indicate the occurrence of a relatively slow, thermally activated motion. In order to assist the determination of the nature of the motion, it is worthwhile to consider the ^{14}N NQR results[4] and ^{1}H NMR data together; at first, the discussion will be restricted to the low-temperature phase, (below about 29°C). In this phase, three observed transitions could be interpreted[4] as arising from a single type of crystallographic site for all ^{14}N nuclei; the quadrupole coupling constant (e^2qQ/h) and asymmetry factor η had values at 77°K of 4857 kHz and 0.536, respectively. The principal axes of the electric field gradient (efg) tensor seen by the ^{14}N nuclei were aligned as follows: QZ along the N-N direction, OX in the molecular plane, and OY perpendicular to the molecular plane. (It was this finding which guided the choice of molecular axes for the crystal energy calculations described in the present work).

The minimum observed in the T_{1D} curve (Figure 1) indicates that molecular reorientations with correlation times $\tau_c \sim 10^{-5}$ sec are occurring at about 305 K; it is now assumed that this estimate of τ_c is also of the correct order of magnitude for below the phase transition (<300 K). The fact that NQR spectra are clearly observable, albeit with some degree of experimental difficulty,[4] despite such a short correlation time, calls for some comment. For example, the ^{14}N NQR signals from *s*-triazine were observed[21] to fade out at about 280 K, where the correlation time for the motion was 6–12 × 10^{-5} sec; signals from pyrazine, on the other hand, were observable[4] up to the melting point, where the correlation time may be estimated from the present proton T_{1D} data to be ~2 × 10^{-6} sec.

One possible explanation of this apparent discrepancy could be based upon differences in purity; no details of sample preparation were given for the NQR experiments.[4] In the present work, fractional sublimation of the pyrazine produced no observable effect upon the T_1 data. However, if the main impurities were isomeric diazines such a procedure, as was also used previously,[3] might not have been very effective in practice; mass spectrometry yielded no significant differences between sublimed and untreated samples.

If, as seems probable, the pyrazine sample used in the present work was of a level of purity comparable to that used previously,[2–4] the apparent discrepancies (described above) between the present proton NMR T_1 results and the NQR[4] and infrared and Raman[3] data, are unlikely to be explicable on this basis. Accordingly, an alternative explanation must be sought. The only motion compatible with both the ^{14}N NQR data[4] and the ^{1}H NMR data appears to be a 180° in-plane flip of the molecule between equivalent sites. Such a flipping motion about an axis (OY) which coincides with one of the efg principal axes leaves unaltered the ^{14}N NQR energy levels, thus accounting for the observed[4] NQR spectral pattern in the low-temperature phase, corresponding to a single lattice site for the ^{14}N nuclei; this is also a requirement of the observed[1] low-temperature crystal structure in which the two molecules in the unit cell are crystallographically equivalent.

In principle, measurements of the second moments of the ^{1}H NMR absorption lines can distinguish between motions with $r = 2$ and those with $r > 2$, where r is the number of sites available to the molecule in a complete (360°) rotation. Unfortunately, preliminary measurements indicate that the high-temperature limit for the second moment, where such a distinction would be most clearly evident, is not reached for pyrazine before the melting point.[22]

Accordingly the only additional evidence, relating to this suggestion of a 180° in-plane flip for the motional process in low-temperature crystalline pyrazine, comes from the potential energy calculations, (Figures 2–4). Such calculations, based upon the atom-atom approximation to the intermolecular forces, are subject to considerable error, but the more qualitative features of the results should be valid. Thus, the calculations confirm a 180° in-plane flip as the most likely motional process, with possibly a *very* brief pause at 90° from the stable configuration. Nonetheless, the extraordinary freedom of motion predicted for the two orthogonal directions suggests that large-amplitude librations about the OX and OZ axis could also contribute to the degradation of magnetic to lattice thermal energy. Such a mechanism would not, however, possess a well-defined activation energy; there is no evidence in Figure 1 for a major contribution from such a mechánism, particularly in view of the symmetry of the T_{1D} curve. Moreover, such large-amplitude librations usually do not provide an effective ^{1}H dipolar relaxation mechanism since they take place at infrared frequencies. However, such librations could certainly affect the ^{1}H second moments and the ^{14}N NQR frequencies, as well as the X-ray diffraction results.

Such in-plane motions leave unaltered the orientation of the large electrical quadrupole moment associated with the negatively charged π-electron clouds sandwiching the positively charged atomic framework with its σ bonds; this contribution to the electrostatic intermolecular interaction is completely ignored in the present model,[6,8] though charge asymmetry within the molecular plane is accounted for explicitly. Thus, energy *differences* for *in-plane* motions are probably the most reliable predictions to be derived from the present approximate method of calculating potential energy profiles for planar aromatic molecues in crystals. Even so, the highly empirical nature of the method is emphasized by its ability to absorb the recently discovered[17] error of a factor of two in computed activation energies, by switching to an alternative parametrisation.[18] Thus, the calculated profiles (Figures 2–4) should be accepted only for their qualitative shapes, with semi-quantitative indications of barrier heights. Even within this context, however, the calculations clearly support the present suggestion of a 180° in-plane flip as the motional process occurring in the low-temperature phase of pyrazine.

The computed lattice energy, which is *not* subject to the above mentioned factor of two,[17] was 11–12 k cals mol^{-1}, appreciably lower than the experimental value of 13.45 k cals mol^{-1} obtained[23] for the sublimation enthalpy; this discrepancy is outside the usual[6,7,8,13] deviation of $\pm 10\%$ for the parameter. Although no value was explicitly given[23] for the temperature at which the sublimation enthalpy was determined, the apparatus used[23] was previously described[24] as being designed for operation at 25°C; thus, the experimentally determined sublimation enthalpy almost certainly refers to the low temperature phase. The low value calculated by the present method is probably to be ascribed to accumulated errors in the model, particularly those associated with the representation of the nitrogen atom with its lone pair.

(b) Transition to high temperature phase

A striking feature of the T_1 and T_{1D} data plotted in Figure 1 is that they display no sign of a discontinuity at either of the temperatures at which transitions were observed using other techniques.[2-4] In what follows, the transition observed at about 29°C will be emphasized, since it shows up in the data for each of the heat capacity,[2] infrared and Raman spectra,[2,3] observations of the crystalline phase with a polarising microscope,[2] and in the ^{14}N NQR results. The transition at 35°C was apparent only in the ^{14}N NQR data, and even so was a less dramatic discontinuity than that observed by the same technique[4] at 29°C.

The splitting of the ^{14}N NQR lines above 29°C suggests[4] that the ^{14}N atoms may now occupy more than one type of site in the lattice. The observations with the polarising microscope[2] suggest that the transition involves some simple reorientation of the molecules at fixed lattice sites, leaving unaltered the orientation of the crystal axes. The infrared spectra in polarised light[3] confirm this finding, and further require a crystal structure above 29°C with the unit cell containing two molecules on C_{2h} sites.[3] The nature of the transition suggested previously[3] involved rotation of molecules around their N-N axes, yielding a "fish-bond" packing typical of benzene for example, instead of the parallel packing observed[1] for pyrazine below 29°C. It is not clear to what extent this suggestion could account for the splitting[4] of the ^{14}N NQR lines; further, the potential energy profile of Figure 3, while not entirely reliable for reasons discussed above, shows no qualitative feature suggesting that such a change might lead to a stable configuration.

On the other hand, the potential energy profile for in-plane rotation (Figure 2) displays a sub-minimum at 90° rotation, corresponding to a metastable configuration. This seems rather surprising at first, since the pseudo C_6 molecular symmetry might predict sub-minima every 60° or so. However, the occurrence of the sub-minimum at 90° may be qualitatively explained in terms of the observed crystal structure[1], which involves a very close contact of 0.2067 nm between each (assumed spherical) nitrogen atom and a hydrogen atom on a neighbouring molecule. The distance between the "conceptual" hydrogen atom representing the lone pair on the nitrogen, and the real hydrogen atom bonded to a carbon on the neighbouring molecule, is thus about 0.19 nm, which is very short. However, if the test molecule is rotated by 60°, replacing the "conceptual carbon-hydrogen" group, with a bond-length of 0.07 nm, by a *real* carbon-hydrogen group with a bond length of 0.108 nm, this contact is reduced to 0.16 nm, which corresponds to an extremely large repulsive energy on the exponentially increasing repulsive portion of the potential curve. This very close contact dominates the interaction, and the sub-minimum observed at 90° rotation represents the orientation in which the two real hydrogen atoms straddle the projecting hydrogen atom on the neighbouring molecule. (The double-minimum at the crystallographic orientation, noted above (Figure 2), is the residual effect obtaining when it is the "conceptual carbon-hydrogen" group, representing the nitrogen atom with its lone pair, which is involved in the interaction.)

As a first attempt to exploit this sub-minimum in the potential energy profile for in-plane rotation, a lattice was considered in which all molecules were rotated by 90° from the crystallographic orientations determined[1] for the low temperature phase. The potential energy profile obtained for in-plane rotation of a pyrazine molecule in such a lattice is shown in Figure 5; a minimum, of approximately the correct depth to account for the sublimation enthalpy,[20] is observed every 90° or so. However, this proposal is not self-consistent, since the lattice surrounding the test molecule, (whose potential energy profile is that shown in Figure 5), consists of pyrazine molecules in just one uniquely determined orientation; thus, only 180° flips, not 90° jumps, would be consistent with the chosen crystal structure, for molecules *other* than the central test molecule.

It was thought that perhaps a disordered structure, in which the pyrazine molecule at each lattice site would have equally available two orientations, related by a 90° in-plane rotation, could account for all the observed data. Thus, the transition at 29°C would be an order-disorder transition, and would be anticipated to have an excess entropy change for the transition of $R \ln 2 = 1.38$ cals deg^{-1} mol^{-1}, since each molecule would have two available distinguishable orientations above 29°C, and only one below. The observed[2] enthalpy change of 263 cals mol^{-1} corresponds to an entropy of transition of only some 0.85 cals deg^{-1} mol^{-1}; however, the differential scanning calorimeter technique used[2] is susceptible to underestimating enthalpy changes, if the transitions are slow relative to the temperature scanning rate.

Accordingly, such disorder was introduced to the lattice through use of a random number generator, as described previously[8] for the cases of thiophene and furan. Several disordered lattices were thus generated, to ensure that the corresponding computed potential energy profiles were typical, and not accidentally chosen to be unrepresentative. Unfortunately, each profile thus generated showed a potential minimum only every 180° of rotation; the subminimum at 90° rotation (Figure 2) either disappeared completely or was reduced to an extremely shallow dish. Thus, this model lattice is not self-consistent either, since forcing the surrounding molecules into a two-fold disorder should have yielded a potential energy minimum for the central test molecule after each 90° rotation.

Finally several ordered packing patterns were investigated. All were based upon an orthorhombic lattice, with the cell parameters determined[1] for the low-temperature phase. In addition, the following conditions must be met by any proposed structure:

i) There must be at least two distinguishable sites for the ^{14}N nuclei, to account for the NQR spectra.

ii) The barrier to in-plane rotation must be similar, in both shape and height, to that computed for the low-temperature phase; then, the lack of an observable discontinuity in the present T_1 results (Figure 1) could be accounted for.

A model lattice in which one of the molecules in the unit cell remains in the low-temperature orientation, while the second occupies an orientation reached by an in-plane rotation of 90°, yielded the potential energy profile for the test molecule shown in Figure 6. Within the limits of error imposed by the approximate potential functions used here, this proposed crystal structure appears to satisfy conditions i) and ii) above. This proposal is possibly not unique, but appears to provide the basis for a self-consistent explanation of the observed transition.

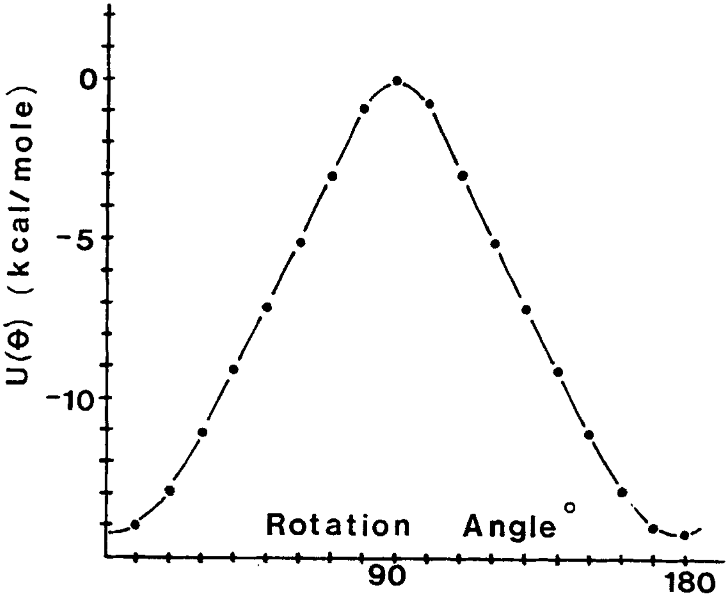

FIGURE 6 Potential energy profile for in-plane rotation of a pyrazine molecule in a model lattice generated from the low-temperature lattice by an in-plane rotation by 90 degrees of the molecule centred at the origin of the unit cell, while the second molecule remains in the low-temperature orientation.

Thus, this is presently visualised as an isothermal, (or almost so), transition from the ordered low-temperature structure[1] to another ordered structure, related to the first by a 90° in-plane rotation of one of the molecules in the unit cell. There are thus two distinct sites for the ^{14}N nuclei in the high-temperature structure, which is nonetheless very similar to the low-temperature form. Moreover, the height and shape of the potential energy barrier to a 180° in-plane flip are not too different from those computed (Figure 2) for the low-temperature structure; thus, it is conceivable that the transition could take place without significant discontinuities in the T_1 curves (Figure 1). In view of the experimental difficulties experienced in measuring the long relaxation times observed, relatively small discontinuities could have been undetected within the experimental scatter, (Figure 1). It appears also that this proposal meets the criteria stated[3] to be necessary for consistency with the infrared and Raman data.

The additional NQR discontinuity observed[4] at 35°C remains a mystery. Possibly a careful search by other techniques could also detect a second transition; for example, the highest temperature used in the infrared study[2,3] was stated to be 35°C. Possibly upward extension of the temperature range by a few more degrees might reveal a further discontinuity in the infrared spectra. In view of the lack of experimental information concerning this additional transition, however, speculation on its nature was not considered to be justified.

V CONCLUSIONS

The ^1H NMR data, and theoretical calculations of molecular energies within the lattice, presented here, appear to fit in reasonably well with previous data available for the low-temperature form of crystalline pyrazine, (viz. X-ray crystal structure data,[1] infrared and Raman data,[2,3] and ^{14}N NQR spectra[4]), if the 180° in-plane flip is accepted as the motional process involved. However, the NMR results display no observable trace of the phase transition previously observed [2-4] at 29°C, nor of the additional transition observed[4] only in the NQR results at 35°C. This is clearly an observation of some significance for the nature of the transitions, particularly that at 29°C. The present proposal to account for these observations in terms of a simple change in molecular orientation within the crystal structure should be tested experimentally, preferably by further X-ray diffraction studies at carefully controlled temperatures, e.g. at (32 ± 1)°C, and at >35°C.

The present work also illustrates the usefulness of the simple atom-atom approximation to intermolecular forces in crystals, provided that the physical meaning of the approximations involved, and the consequent limits of validity, are always kept in mind. Even for the molecular crystal of such a simple species as pyrazine, the gaps in understanding are sufficient that the approach can yield valuable insights.

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