(2)

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

EPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
ECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION / AVAILABILITY OF REPORT Aproved for public release; distribution unlimited.
ECLASSIFICATION / DOWNGRADING SCHEDULE Unclassified	
RFORMING ORGANIZATION REPORT NUMBER(S) N00014-79-C-0647	5. MONITORING ORGANIZATION REPORT NUMBER(S)
AME OF PERFORMING ORGANIZATION Colorado State University / 6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
DRESS (City, State, and ZIP Code) Department of Chemistry Fort Collins, CO 80523	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research / 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-79-C-0647
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
"Determination of the Minimum Energy Conformation of Alkyl Substituted Pyrazines"

12 PERSONAL AUTHOR(S)
Hoong-Sun Im, E. R. Bernstein & J. I. Seeman

13a TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical Report	FROM _____ TO _____	December 15, 1989	

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
methyl substituted pyrazines, ethyl substituted pyrazines, isopropyl substituted pyrazines, n-propyl pyrazines, mass resolved excitation spectroscopy, supersonic jet cooled molecules, internal hydrogen bonding, conformations of substituted molecules, structure

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

SEE ATTACHED ABSTRACT

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Elliot R. Bernstein	22b. TELEPHONE (Include Area Code) (303) 491-6347 / 22c OFFICE SYMBOL

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0647

TECHNICAL REPORT #67

"Determination of the Minimum Energy Conformation of Alkyl Substituted Pyrazines"

by

Hoong-Sun Im, E. R. Bernstein and J. I. Seeman

To be submitted for publication in Journal of American Chemical Society

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

December 15, 1989

DETERMINATION OF THE MINIMUM ENERGY CONFORMATION OF ALKYL SUBSTITUTED PYRAZINES

Hoong-Sun Im and E. R. Bernstein

Department of Chemistry
Colorado State University
Fort Collins, CO 80523

and

H. V. Secor, J. Payne, and J. I. Seeman

The Philip Morris Research Center
P.O. Box 26583
Richmond, VA 23261

ABSTRACT

Conformational preferences for methyl, ethyl, isopropyl and n-propyl substituted pyrazines are determined by mass resolved excitation spectroscopy for the supersonic jet cooled molecules and MOPAC 5.0 semi-empirical conformational calculations. The results of these studies suggest that the behavior of the alkyl substituted pyrazines is very different from that of alkyl substituted benzenes. This difference is caused by substantial hydrogen bonding between the α-hydrogens of the alkyl substituent and the adjacent lone pair nonbonding electrons on the ring nitrogen atom. One of these hydrogen atoms becomes nearly planar (ca. ±10° according to the MOPAC 5.0 calculation) with the aromatic ring.

I. INTRODUCTION

Supersonic jet laser spectroscopy has been utilized to identify the minimum energy conformers of substituted aromatic molecules in the gas phase. These determinations have been performed based on the observation that each conformer produces its own origin $\left(0_0^0\right)$ transition for the $S_1 \leftarrow S_0$ excitation. Thus the counting of origin transitions in the mass resolved excitation spectrum reveals the number of conformers present for a given system. Molecules studied in our laboratory thus far center around substituted benzenes - alkyl substituted benzenes[1], methoxy benzene[2], allyl benzene[3], and styrenes.[4] The rotational isomers of phenol and β-naphtol have also been determined by this technique as well.[5] These studies have increased our understanding of the conformations of substituents with respect to an aromatic ring in a systematic fashion.

This paper extends these conformational studies to N-heterocyclic aromatic molecules which are similar to the benzenes in that they are monocyclic aromatics, but which differ from benzenes in the composition of the ring. In these systems, one of the ring C-H groups adjacent to the substituents is replaced by a nitrogen atom and the lone-pair electrons on it. The effect of this change on stable molecular conformations has not been generally studied theoretically or experimentally. Only methyl conformation with respect to the -CH=NH (imine) functionality has been considered theoretically.[6] This latter theoretical study has concluded that the eclipsed conformation is favored over the staggered one in the ground electronic state.

This report presents mass resolved excitation spectra of the $S_1 \leftarrow S_0$ transition of methyl, ethyl, iso-propyl, and n-propylpyrazine and their derivatives in gas phase. The dispersed emission (DE) spectrum of ethylpyrazine is also presented to elucidate the structure of the ethyl conformation. In conjunction with results of MOPAC 5 calculations for the conformational energy of these molecules,[7] the stable conformations of substituted pyrazines can be determined. We demonstrate the following with the above described techniques: the methyl group in methylpyrazine (CH_3-pyz) is determined to be a highly hindered rotor; the ethyl group in ethylpyrazine (C_2H_5-pyz) does not lie in the plane perpendicular to the ring plane but is in an anti-gauche conformation; iso-propylpyrazine (iso-C_3H_7-pyz) has only one stable conformer, in which an α-hydrogen is directed toward the ring nitrogen atom and is nearly in the plane of the ring; and the n-propyl group in n-propylpyrazine (n-C_3H_7-pyz) has two stable conformers -syn and anti gauche - for the terminal methyl group of the propyl moiety.

These results are quite different from those obtained for benzene systems and thus the interaction of a nitrogen atom and its non-bonding electrons with ring substituents differs significantly from that of the C-H group with the same substituents. This behavior can be explained in terms of the internal hydrogen bonding between an α-hydrogen and the lone-pair electrons on a nitrogen atom in the pyrazine systems.

II. EXPERIMENTAL PROCEDURES

All the spectra are obtained using two-color, two photon ionization with time-of-flight mass detection. The time-of-flight mass spectrometer (TOFMS) chamber is described elsewhere.[8] A pulsed molecular jet is employed using an R. M. Jordan pulsed valve. All the samples are placed inside the valve head and heated to about 60°C to increase their concentration in the beam. In all cases, He is used as the carrier gas at roughly 50 psig. Two Nd^{+3}/YAG lasers are used to produce excitation and ionization photons. The doubled output of DCM dye is employed for the $\pi^* \leftarrow n$ excitation of alkyl substituted pyrazines and the doubled output of R590 dye mixed with the residual 1.064 μm Nd^{+3}/YAG beam is used to provide the ionization photon.

Dispersed emission (DE) experiments are performed in a fluorescence excitation (FE) chamber described previously.[8] f/4 optics are used to collect and focus the emission onto the slits of an f/8 2051 GCA McPherson monochromator. Spectra are recorded with a 1200 groove/mm, 1.0 μm blazed grating in the third order. Expansion of the gas into the chamber is achieved with a cw nozzle with 100 μm pinhole. Samples are placed inside the gas line and heated to 60°C to achieve a greater concentration in the jet. He is employed as the carrier gas at a pressure of ~30 psig.

All samples are synthesized at Philip Morris USA Research Center except for methylpyrazine (CH_3-pyz) which is obtained from Aldrich. All samples are studied as received and not further purified.

Stable geometries of various alkyl substituted pyrazine systems are calculated using the MOPAC (v.5.0) programs. MOPAC (v. 5.0) programs have two Hamiltonians available for structure calculations: PM3[9] and AM1[10]. The PM3 Hamiltonian has been augmented and improved for hetero atom (N,O, etc.) calculations. All calculational results reported in this work are based on the PM3 Hamiltonian. Input data for the calculations are obtained from pyrazine[11] and normal alkane[12] crystal structures.

III. RESULTS

A. Methylpyrazine

The TOFMS of CH_3- pyz and CD_3-pyz are displayed in Figures 1a and 1b, respectively. The origin of the $S_1 \leftarrow S_0$ transition of CH_3-pyz occurs at 30945.3 cm^{-1}. The peak at 358.2 cm^{-1} to higher energy of the origin is assigned as ν_{13}.[13] Between these two peaks - the origin and ν_{13} - several weak features appear in the absorption spectrum. The TOFMS of CD_3-pyz contains a single origin at 30937.7 cm^{-1}, and one strong feature at 363.0 cm^{-1} to the blue of the origin. The latter feature is assigned as ν_{13} in this molecule. Upon deuteration of the methyl group, most of the weak features shift to higher energy or not at all. Only the first weak doublet peak shows a significant, typical isotope effect upon methyl deuteration. From an expansion pressure study for both CH_3-pyz and CD_3-pyz, however, this doublet feature can be characterized as a vibrational hot band (see Figures 2 and 3). Absence of a normal isotope effect on the cold bands implies that none of these cold features are associated with methyl rotor transitions.

B. ETHYLPYRAZINES

1. Ethylpyrazine

The TOFMS of C_2H_5-pyz about the origin region of the $S_1 \leftarrow S_0$ transition is presented in Figure 4. This spectrum can be interpreted in one of two ways: the spectrum consists of one origin and a series of vibronic features built on it; or the spectrum consists of two origins - the first two peaks - and two series of vibronic features built on them. In order to choose between these two spectroscopic assignments, DE studies are performed for this molecule.

Figure 5 depicts the DE spectra of ethylpyrazine excited at 30856.8 cm^{-1} (0_0^0 - marked A in Figure 4) and at 30918.6 cm^{-1} ($0_0^0 + X_0^1$ - marked B in Figure 4). Both spectra show the same spacing (40 cm^{-1}) of vibrational progressions built on the excitation line. This observation implies that the peak marked B in Figure 4 is a member of the vibrational progression built on the origin at 30856.8 cm^{-1}. If the feature at $0_0^0 + X_0^1$ were a new origin of a different ethylpyrazine conformation, one would not expect the

emission spectra arising from the two excitations (0_0^0 and $0_0^0 + X_0^1$) to be so similar. The data and assignments for the absorption spectrum are collected in Table I. Since only one origin is observed, only one stable conformer of C_2H_5-pyz exists in the ground state.

2. 2,6-di-Ethylpyrazine

Figure 6 shows the TOFMS of jet cooled 2,6-$(C_2H_5)_2$-pyz about the origin region of the $S_1 \leftarrow S_0$ transition. Two origins are displayed at 30951.3 and 30964.9 cm^{-1}. The same vibronic features found in the spectrum of C_2H_5-pyz also appear to be built on both of these origins. Since two origins are observed, this molecule has two stable conformers in the ground state.

C iso-Propylpyrazines

1. iso-Propylpyrazine

The TOFMS of jet cooled iso-C_3H_7-pyz is depicted in Figure 7. Only one intense origin is observed (at 30793.3 cm^{-1}) in the spectrum of this molecule. Thus only one stable conformer exists for this molecule in the ground state.

2. 6-Methyl-2-iso-propylpyrazine

Figure 8 displays the TOFMS of jet cooled 6-CH_3-2-iso-C_3H_7-pyz around the origin region of the $S_1 \leftarrow S_0$ transition. The absorption spectrum of 6-CH_3-2-iso-C_3H_7-pyz contains only one origin with several weak features due to methyl group rotations built on it. This observation also implies that only one stable conformer exists for 6-CH_3-iso-C_3H_7-pyz in the ground state.

D n-Propylpyrazines

1. n-Propylpyrazine

The TOFMS of n-C_3H_7-pyz and its partially deuterated isotope, n-C_3D_7-pyz, are presented in Figures 9a and 9b, respectively. Only two peaks (marked as A and A') among the features in the spectra do not show any isotope effect at all. Other features

show approximately a 5% isotope effect (B, C, D, E) or a 9% isotope effect (B', C', D'). These data are collected in Table II. The two peaks (at 30782.3 and 30882.0 cm^{-1}) in the TOFMS of n-C_3H_7-pyz which have no relative isotope effect (E_A- $E_{A'}$ = 70 cm^{-1}) are assigned as origins.[14] The peaks marked B, C, D and E are assigned as the torsinal mode vibrational progression of the n-propyl group built on origin A and those marked B', C', and D' are assigned as a similar torsinal mode vibrational progression built on origin A'. The observations of two origins implies that two stable conformers exist for the ground state of n-C_3H_7-pyz.

2. 6-Methyl-2-n-propylpyrazine

Figure 10 displays the TOFMS of jet cooled 6-CH_3-2-n-C_3H_7-pyz about the origin region of the $S_1 \leftarrow S_0$ transition. Like the TOFMS of n-C_3H_7-pyz, this spectrum shows two origins (at 30984.3 and 31059.8 cm^{-1}) with the same vibrational progressions built on them. Several other weak features due to methyl substitution can be observed in the spectrum as well. Since two origins are observed, one can confirm that this molecule also has only two stable conformers in the ground state.

IV. DISCUSSION

A. Methyl torsion

The TOFMS of methylpyrazine does not evidence methyl rotor transitions; on the other hand, the TOFMS of toluene evidences intense methyl free rotor transitions in its origin region.[1(a)] This difference must arise from the difference of the composition of the ring: replacement of the ring C-H group with a nitrogen atom and non-bonding electrons must change the potential energy barrier for methyl torsion.

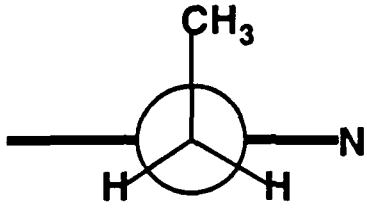
Since no methyl torsinal transitions are observed, one can not readily discern whether the potential barrier has increased or decreased for methylpyrazine with respect to that for toluene. Considering the possibility of an internal hydrogen bonding interaction between the methyl hydrogens and the lone-pair electrons, however, one can suggest that the potential barrier has increased in methylpyrazine over that found for toluene. This interpretation, which at this point in the discussion is only a working hypothesis, will be supported by results for the other systems studied.

B. Stable conformations of alkyl substituted pyrazine

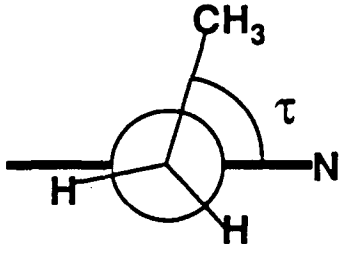
1. Ethylpyrazine

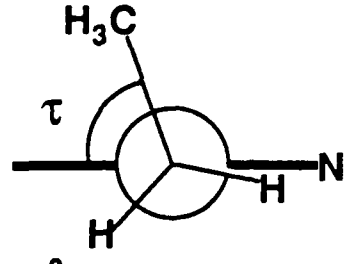
As shown in Scheme I, several conformers are possible for C_2H_5-pyz: perpendicular, gauche and planar with respect to the position of methyl end group of the ethyl substituent. In this molecule, unlike ethyl benzene all five possible conformers would have different energies. Of course, only one of these five possible conformers is physically realized.

Scheme I



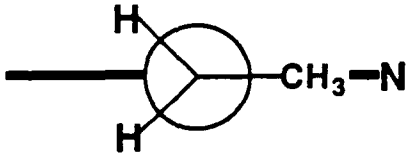
perpendicular

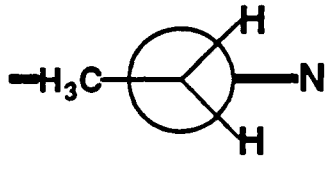




$0^0 < \tau < 90^0$

syn-gauche **anti-gauche**





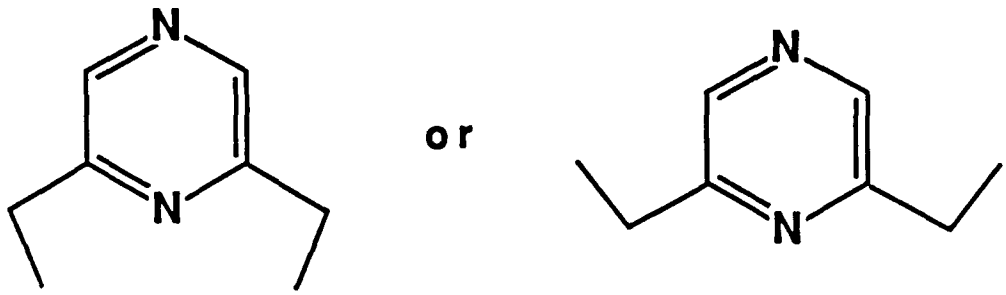
planar

E_{ex} = 30856.8 cm-1, 0_0^0

E_{ex} = 30918.6 cm-1, $0_0^0 + X_0^1$

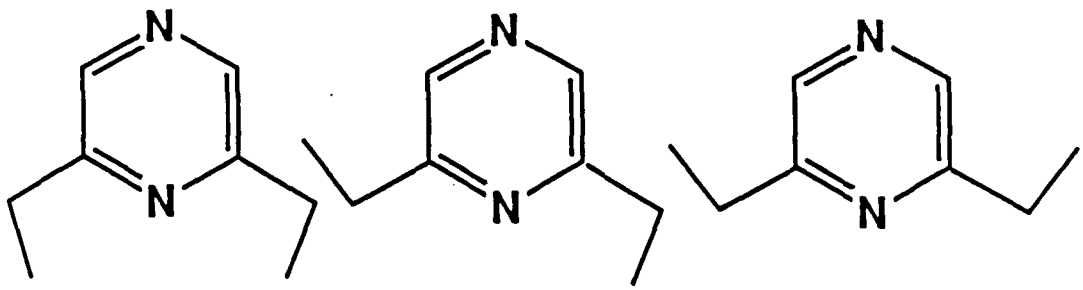
The observation of two origins in the TOFMS of 2,6-diethylpyrazine excludes the possibility of the planar conformer as the stable one because only one origin should be observed if only one of the planar conformers is stable (see Scheme II).

Scheme II



[Three origins should be observed if two planar conformers were to exist (see Scheme III).]

Scheme III



The next possibility for the stable conformation of ethylpyrazine is the perpendicular one. Even though this conformer is consistent with the observed spectra of the ethylpyrazines, it is only an actual possibility if the interaction of the ethyl substituent with the ring is symmetrical. This interpretation, however, is not consistent with the observations for methylpyrazine. The perpendicular conformer must thereby also be excluded. The

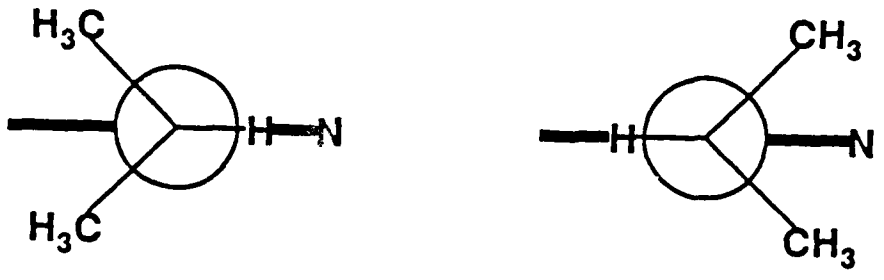
observations can be explained if only one gauche conformer exists as the minimum energy conformation for ethylpyrazine. A single gauche conformation for ethylpyrazine is consistent with the experimental observations: one origin for ethylpyrazine, two origins for 2,6-diethylpyrazine, and the asymmetric interaction of the substituent with the ring.

From the experimental results, one cannot predict which gauche form is stable. Determination of the stable conformer for ethylpyrazine is made through MOPAC 5 calculations. The anti-gauche conformer (Scheme I) is determined to be the minimum energy conformer; the torsinal angles τ_1 (C_{ortho}-C_{ipso}-C_α-C_β) = 72° and τ_2 (N-C_{ipso}-C_α-H_α) = 12°. The cause of this asymmetry in ethyl orientation for ethylpyrazine, that is the non-perpendicular geometry, is thus internal hydrogen bonding between one hydrogen of the α-CH_2 moiety and the adjacent nitrogen lone-pair electrons. Figure 11 contains a detailed picture of this chosen structure.

2. iso-Propylpyrazine

The conformation of iso-propylbenzene for which the α-hydrogen is in the plane of the ring has been determined to be the stable minimum energy conformation.[15] From this result, one of the two conformers shown in Scheme IV can be considered as the single stable conformation of iso-propylpyrazine.

Scheme IV



1 2

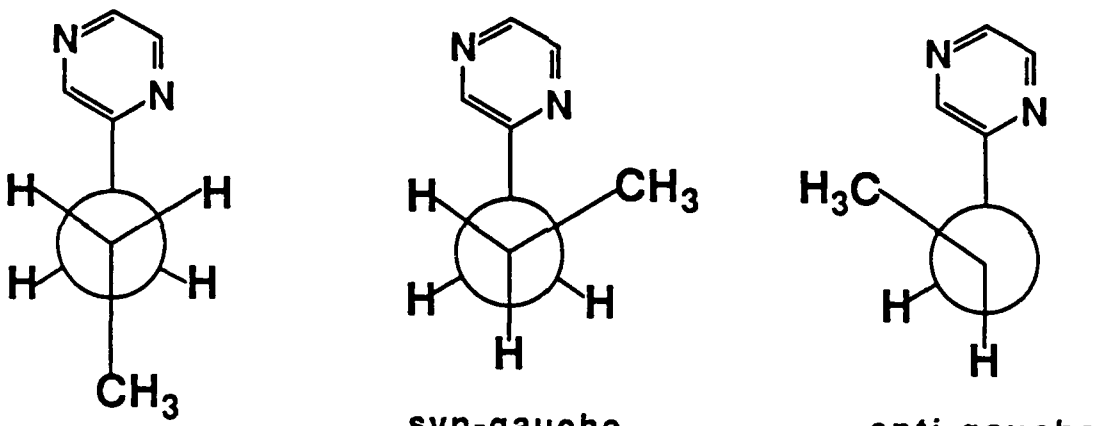
Because of the demonstrated asymmetric interaction of the substituent with the ring, these two conformers do not have the same conformational energy. The conformer in which the α-hydrogen is toward the nitrogen atom and in the plane of the ring is

suggested to be the minimum energy conformer based on MOPAC calculations and internal hydrogen bonding interaction considerations (see Figure 11).

3. n-Propylpyrazine

The experimental results for n-C_3H_7-pyz are similar to those for n-propylbenzene[1(c)]: two origins are found in the $S_1 \leftarrow S_0$ mass resolved excitation spectra of both molecules. As seen in Scheme V, however, the situation for n-C_3H_7-pyz is somewhat different from that for n-propylbenzene because of the asymmetric ring/substituent interactions.

Scheme V



The following three possibilities arise for the two assigned origins in the n-C_3H_7-pyz spectrum: 1. anti and one gauche conformers are observed; 2. anti and both gauche (degenerate in energy) conformers are observed; and 3. only both gauche conformer are observed. Most likely only one gauche conformer is observed along with the anti conformer based on the results of MOPAC calculations for other systems and the spectra of 6-CH_3-2-n-C_3H_7-pyz in which only two origins are observed. Due to a "self-solvation" of the aromatic ring by the propyl group which lowers the S_1 energy more than the S_0 energy,[16] the peak at 307823 cm^{-1}(A) in Figure 8a is assigned as the gauche conformer origin. The other origin at 308523 cm^{-1} (A') must then be associated with the anti

conformer. These assignments are consistent with those made for the n-propylbenzene system.[1(c)]

More detailed assignment of n-C_3H_7-pyz geometries must be obtained from MOPAC calculations and through analogy with other alkyl substituted pyrazines studied in this work. τ_1 and τ_2 obtained from ethylpyrazine are expected to be valid for n-C_3H_7-pyz and in fact the MOPAC results give $\tau_1(C_{ortho}\text{-}C_{ipso}\text{-}C_\alpha\text{-}C_\beta) = 77°$, $\tau_2(N\text{-}C_{ipso}\text{-}C_\alpha\text{-}H_\alpha) = 17°$ and $\tau_3(C_{ipso}\text{-}C_\alpha\text{-}C_\beta\text{-}C_\gamma) = 180°$. Gauche conformers have higher calculated conformational energy by ~700 cm^{-1}; the calculations suggest that the two gauche conformers have only a 40 cm^{-1} energy difference. The syn-gauche conformer has torsinal angles of $\tau_1(C_{ortho}\text{-}C_{ipso}\text{-}C_\alpha\text{-}C_\beta) = 69°$, $\tau_2(N\text{-}C_{ipso}\text{-}C_\alpha\text{-}H_\alpha) = 9°$ and $\tau_3(C_{ipso}\text{-}C_\alpha\text{-}C_\beta\text{-}C_\gamma) = 73°$ and the anti-gauche conformer has torsinal angles $\tau_1 = 93°$, $\tau_2 = 33°$ and $\tau_3 = 75°$. The calculation indicates that the anti-gauche conformer is more stable than the syn-gauche conformer. We have a preference for the syn-gauche conformer as the stable gauche conformer of n-C_3H_7-pyz for two reasons: 1. reduced interaction between the terminal propyl methyl group and the ring C-H fragment; and 2. increased hydrogen bonding between the α-hydrogen and the lone-pair electrons on the adjacent nitrogen atom. This reasoning is consistent with the notion of strong asymmetric interaction between substituents and the ring system for alkyl substituted N-heterocycles. These two conformers are depicted in Figure 11.

V. SUMMARY AND CONCLUSIONS

The stable conformations of alkyl substituted pyrazine systems have been determined through the use of supersonic jet laser spectroscopy and MOPAC 5 calculations. The individual stable conformations of the alkyl substituted pyrazines are quite different from those of comparable alkyl substituted benzenes. For example, the methyl group in methylpyrazine shows highly hindered motion of the methyl torsion, the ethyl group is in an anti-gauche conformation, iso-C_3H_7-pyz has a planar internal hydrogen bonded conformation, and one of the possible gauche conformers of n-C_3H_7-pyz is found to be unstable. The detailed information on the geometry of the conformation for each molecule is summarized in Figure 11.

The substituted benzene/pyrazine conformational differences are due to the replacement of one of the ring C-H group with a nitrogen atom and its lone-pair electrons. This change provides the system with a site for internal hydrogen bonding between an α-hydrogen on the substituents and the non-bonding nitrogen electrons. This additional ring/substituent interaction stabilizes the molecular conformations which bring an α-

hydrogen closest to the lone-pair electrons on the nitrogen atom. This interaction is apparently strong enough to produce geometries for the alkyl substituted pyrazine systems, which are different from those of the comparable benzene systems.

Additionally, we have also studied methyl, ethyl and n-propylpyridine.[17] The same conclusions can be drawn for these systems: a highly hindered methyl rotor for methylpyridine, one stable conformer for ethylpyridine and two stable conformers for n-propylpyridine. These observations further confirm the importance of internal hydrogen bonding interactions for the stabilization of alkyl substituted N-heterocycle molecular conformations.

REFERENCES

1. (a) P. J. Breen, J. A. Warren, E. R. Bernstein and J. J. Seeman, J. Chem. Phys. 87, 1917 (1987).

   (b) P. J. Breen, J. A. Warren, E. R. Bernstein and J. J. Seeman, J. Chem. Phys. 87, 1927 (1987).

   (c) P. J. Breen, E. R. Bernstein and J. J. Seeman, J. Chem. Phys. 87, 3269 (1987).

2. P. J. Breen, E. R. Bernstein, H. V. Secor and J. I. Seeman, J. Am. Chem. Soc. 111, 1958 (1989).

3. P. J. Breen, E. R. Bernstein, J. I. Seeman and H. V. Secor, J. Phys. Chem., in press.

4. V. H. Grassian, E. R. Bernstein, H. V. Secor and J. I. Seeman, J. Phys. Chem., in press.

5. A. Oikawa, H. Abe, N. Mikami and M. Ito, J. Phys. Chem. 88, 5180 (1984).

6. A. E. Dorigo, D. W. Pratt and K. N. Houk, J. Am. Chem. Soc. 109, 6591 (1987).

7. This program is obtained from J. J. P. Stewart and J. A. Menapace at the Frank J. Seiler Research Laboratory, USAFA, Colorado Springs, CO.

8. E. R. Bernstein, K. S. Law, and M. Schauer, J. Chem. Phys. 80, 207 (1984).

9. (a) J. J. P. Stewart, J. Comp. Chem. 10, 209 (1989).

   (b) J. J. P. Stewart, J. Comp. Chem. 10, 221 (1989)

10. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. Stewart, J. Am. Chem. Soc., 107, 3902 (1988).

11. P. J. Wheatley, Acta Cryst. 10, 182 (1957).

12. CRC Handbook of Chemistry and Physics, 69th Ed., (CRC Press 1988) p. F-165.

13. G. Herzberg, Molecular Spectra and Molecular Structure III, Van Nostrand Reinhold Company, New York (1966), p. 660.

14. See ref. 2 and 4 and H. S. Im, E. R. Bernstein and J. I. Seeman, J. Am. Chem. Soc., submitted.

15. J. I. Seeman, H. V. Secor, P. J. Breen, V. H. Grassian and E. R. Bernstein, J. Am. Chem. Soc., in press.

16. (a) J. B. Hopkins, D. E. Powers, and R. E. Smalley, J. Chem. Phys. 72, 5039 (1980).

(b) K. S. Law and E. R. Bernstein, J. Chem. Phys. 82, 2856 (1985).

17. H. S. Im, Phd. D. thesis, Colorado State University, 1989.

TABLE I. Energies for C_2H_5-pyz features in the 0_0^0 region of the $S_1 \leftarrow S_0$ transition.

Feature [a]	$\nu - \nu(0_0^0)$ cm^{-1}	Assignment[b]
A	0(30856.8)	Origin
B	61.8	T_0^1
C	116.2	I
D	122.7	T_0^2
E	176.0	$I+T_0^1$
F	183.1	T_0^3
G	207.9	II

a. A through G are the notation of Figure 4 for the observed vibronic features in the absorption spectrum of C_2H_5-pyz.
b. I and II are the notation for undetermined vibrational motions of the molecule and T is the notation for the torsional vibrational motion of the ethyl group.

TABLE II. Energies for n-C_3H_7-pyz and n-C_3D_7-pyz features in the 0_0^0 region of ($S_1 \leftarrow S_0$).

Feature[a]	n-C_3H_7-pyz ν-$\nu(0_0^0)$ cm^{-1}	n-C_3D_7-pyz ν-$\nu(0_0^0)$ cm^{-1}	isotope shift
A	0(30782.3)	0(30787.3)	-
B	48.5	46.1	4.9%
C	97.4	92.4	5.1%
D	145.6	138.3	5.0%
E	193.0	183.0	5.0%
A'	0(30852.0)	0(30857.5)	-
B'	56.0	50.8	9.3%
C'	111.2	100.7	9.4%
D'	-	149.5	-

a. A through E and A' through E' are the notation for the observed vibronic features for each conformer (see Fig. 9).

FIGURE CAPTIONS

Figure 1. TOFMS of jet cooled CH_3- pyz(a) and CD_3-pyz(b) around their 0_0^0 transition regions. Strong origins at 30945.3 and 30937.7 cm^{-1} are found for CH_3- pyz and CD_3-pyz_1, respectively. The next strong peak at 358.2 and 363.0 cm^{-1} for CH_3-pyz and CD_3pyz, respectively, is assigned as ν_{13}. The spectra shown as inserts are taken with low backing pressures (see Figures 2 and 3).

Figure 2. Expansion pressure study of CH_3-pyz. The backing pressures applied are indicated. The two doublets next to the origin show characteristic hot band behavior.

Figure 3. Expansion pressure study of CD_3-pyz. The backing pressures applied are 6.5 psig(a) and 30 psig(b). Again, the peak next to the origin has characteristic hot band behavior.

Figure 4. TOFMS of jet cooled C_2H_5-pyz around its 0_0^0 region. The origin occurs at 30856.8 cm^{-1} and a torsinal progression of the ethyl group is built on it (see Table I). Only one origin is identified in this spectrum.

Figure 5. Dispersed emission spectra of C_2H_5-pyz: a. excitation at 30856.8 cm^{-1}, the feature marked A in Figure 4; b. excitation at 30918.6 cm^{-1}, the feature marked B in Figure 4.

Figure 6. TOFMS of the 0_0^0 region of the ($S_1 \leftarrow S_0$) for jet cooled 2,6-$(C_2H_5)_2$-pyz. The spectrum contains two origins at 30951.3 (syn conformer) and 30964.9 cm^{-1} (anti conformer). The vibronic features built on each origin are also shown.

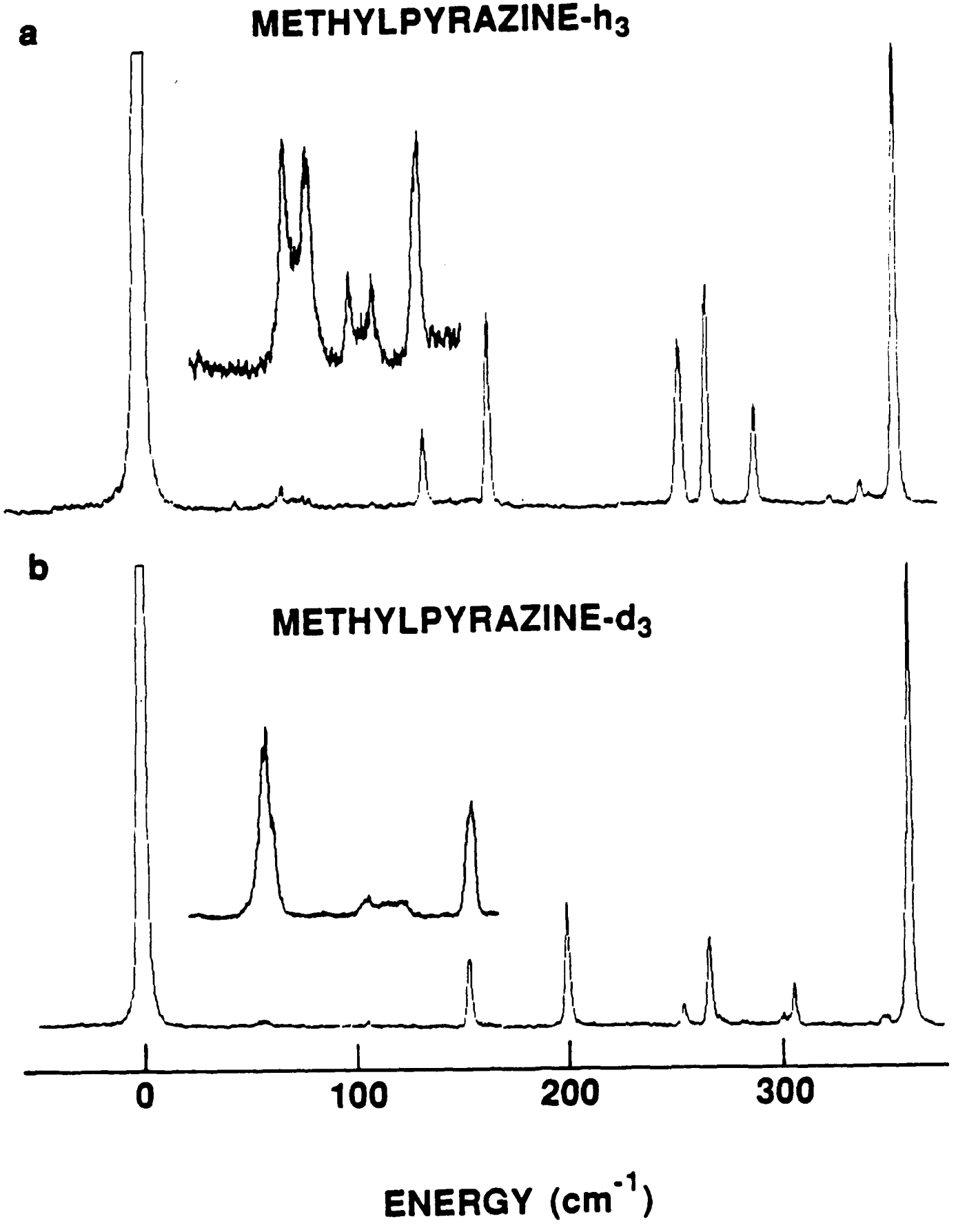
Figure 7. TOFMS of jet cooled iso-C_3H_7-pyz around its origin transition region. The spectrum shows a single intense origin at 30793.3 cm^{-1}.

Figure 8. TOFMS of the 0_0^0 region of ($S_1 \leftarrow S_0$) for jet cooled 6-CH_3-2-iso-C_3H_7-pyz. The single intense feature is assigned as the origin and occurs at 31027.4 cm^{-1}.

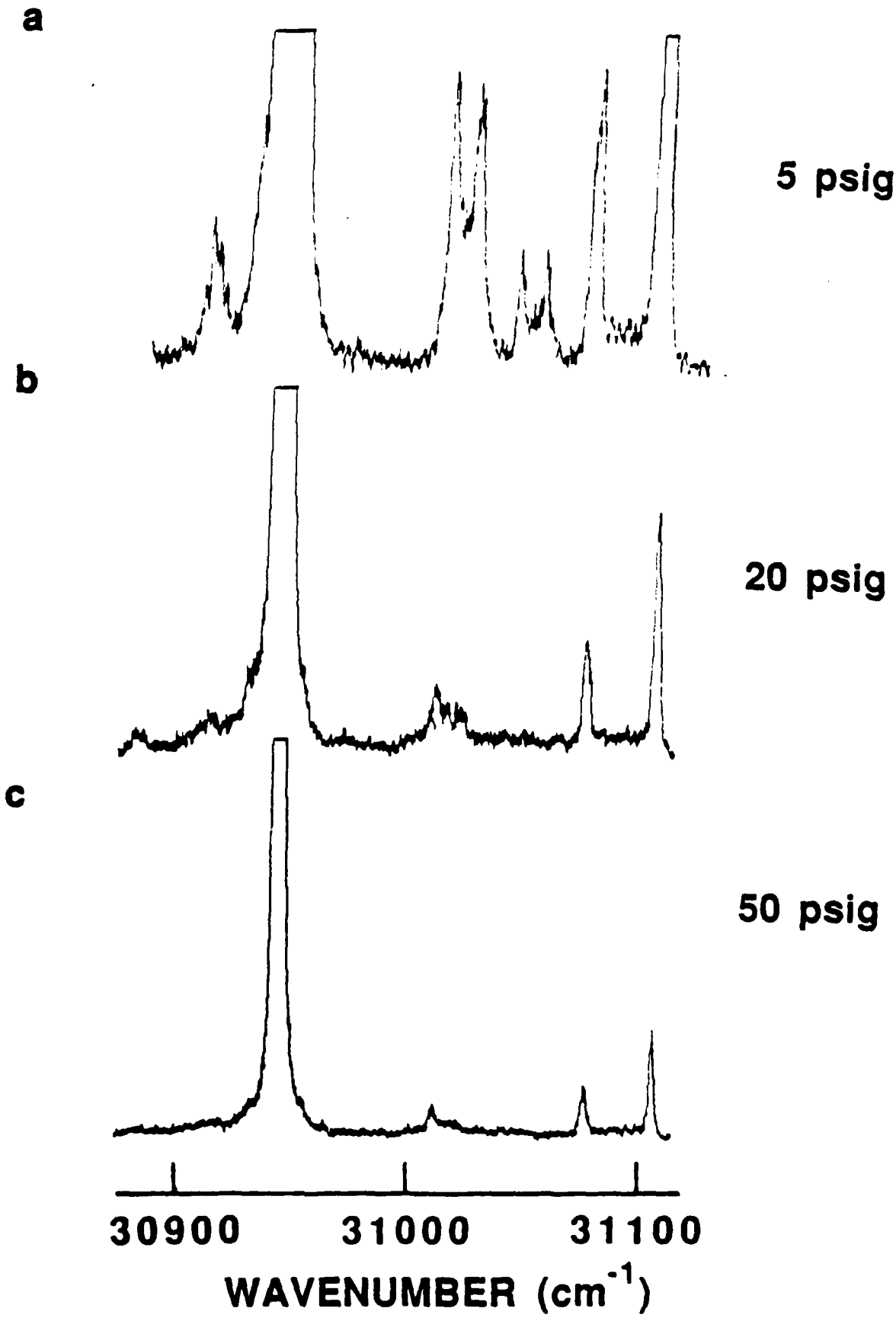
Figure 9. TOFMS of jet cooled n–C_3H_7-pyz(a) and n–C_3D_7-pyz(b) around their 0_0^0 regions. The peaks marked A and A' are assigned as the origins of different conformers based on the absence of a relative isotope effect; the peak marked A is the origin of the syn-gauche conformer and the peak marked A' is for the origin of the anti conformer. (For details see text and Table II.)

Figure 10. TOFMS of jet cooled 6–CH_3-2-n–C_3H_7-pyz around its 0_0^0 region. Two origins are identified - at 30984.3 and 31059.8 cm^{-1}. Torsional vibrational progressions are built on each origin. This spectrum is similar to that of 2-n-C_3H_7-pyz.

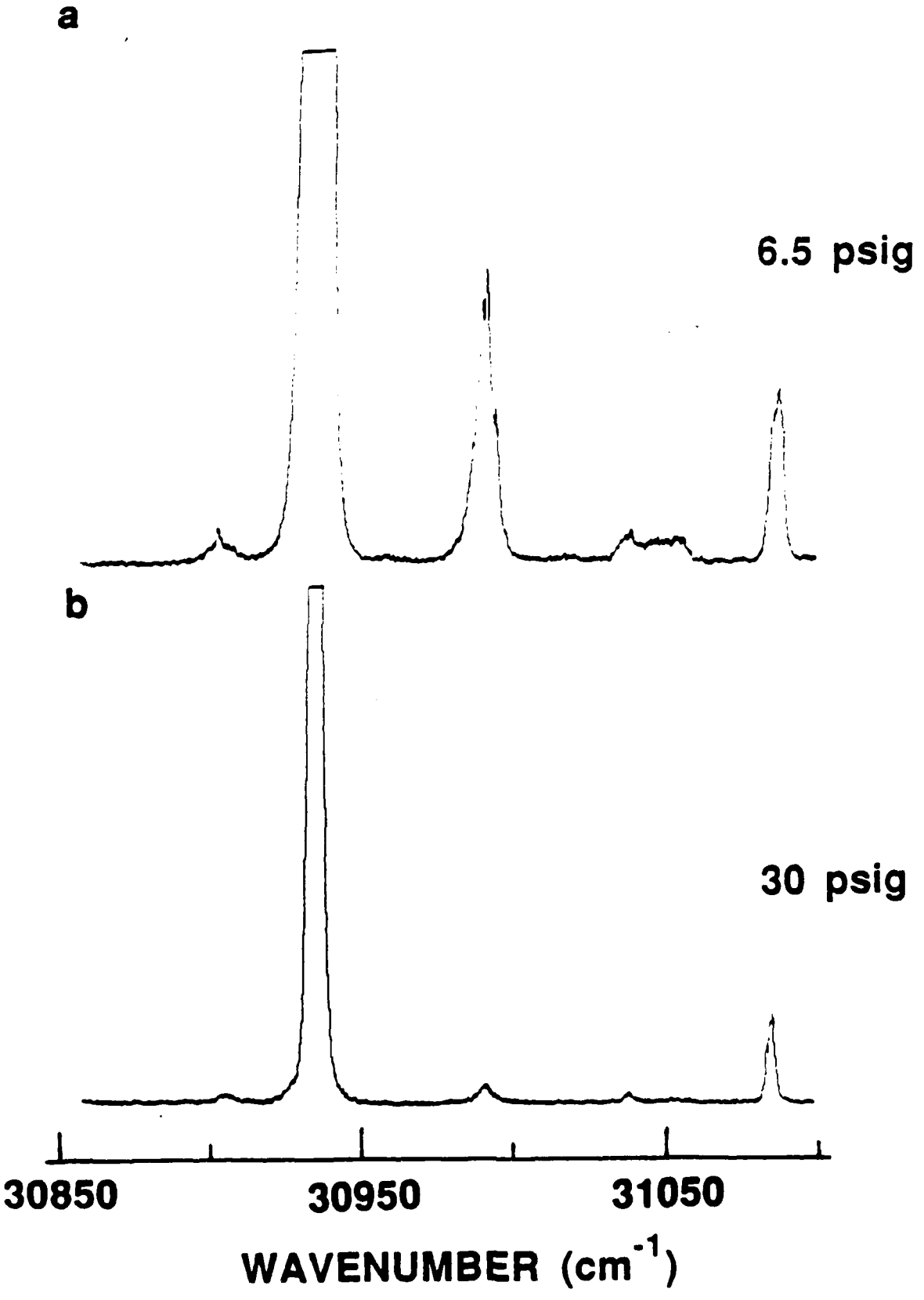
Figure 11. The geometry of the minimum energy conformers for C_2H_5-pyz (a), iso-C_3H_7pyz (b), and n-C_3H_7-pyz (c). The stable conformer of C_2H_5-pyz is determined to have $\tau_1 = 72°$ and $\tau_2 = 12°$. iso-C_3H_7-pyz has a stable conformer in which the α-hydrogen is oriented toward the nitrogen atom and in the plane of the ring ($\tau_2 = 0°$). Two stable conformers of n-C_3H_7-pyz are determined: the anti conformer (I) has $\tau_1 = 77°$, $\tau_2 = 17°$ and $\tau_3 = 180°$; and the syn-gauche conformer (II) has $\tau_1 = 69°$, $\tau_2 = 9°$ and $\tau_3 = 73°$. The geometries of these conformers bring an α-hydrogen closest to the lone-pair electrons on the nitrogen atom.

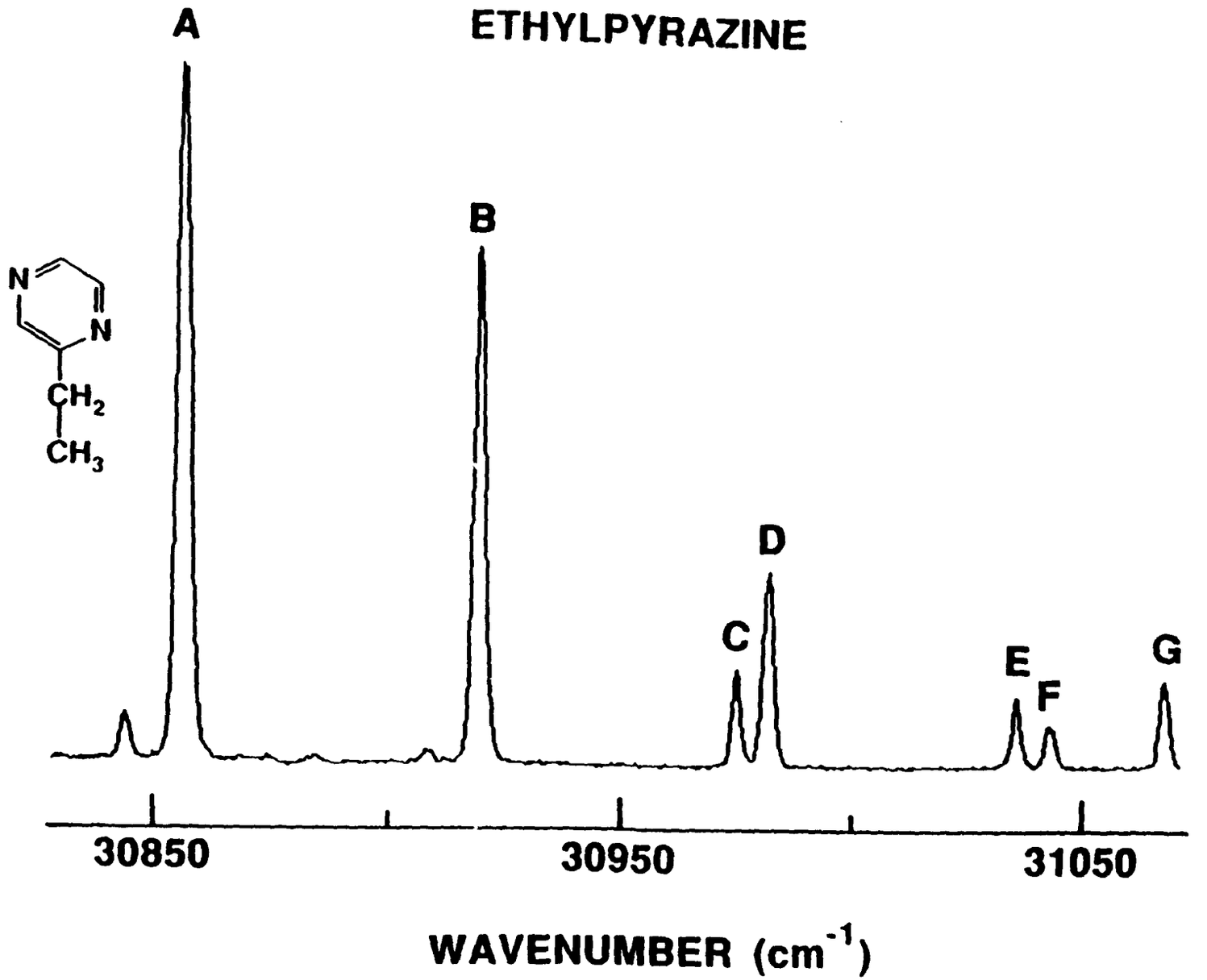

a
METHYLPYRAZINE-h3
b
METHYLPYRAZINE-d3
0
100
200
300
ENERGY (cm-1)

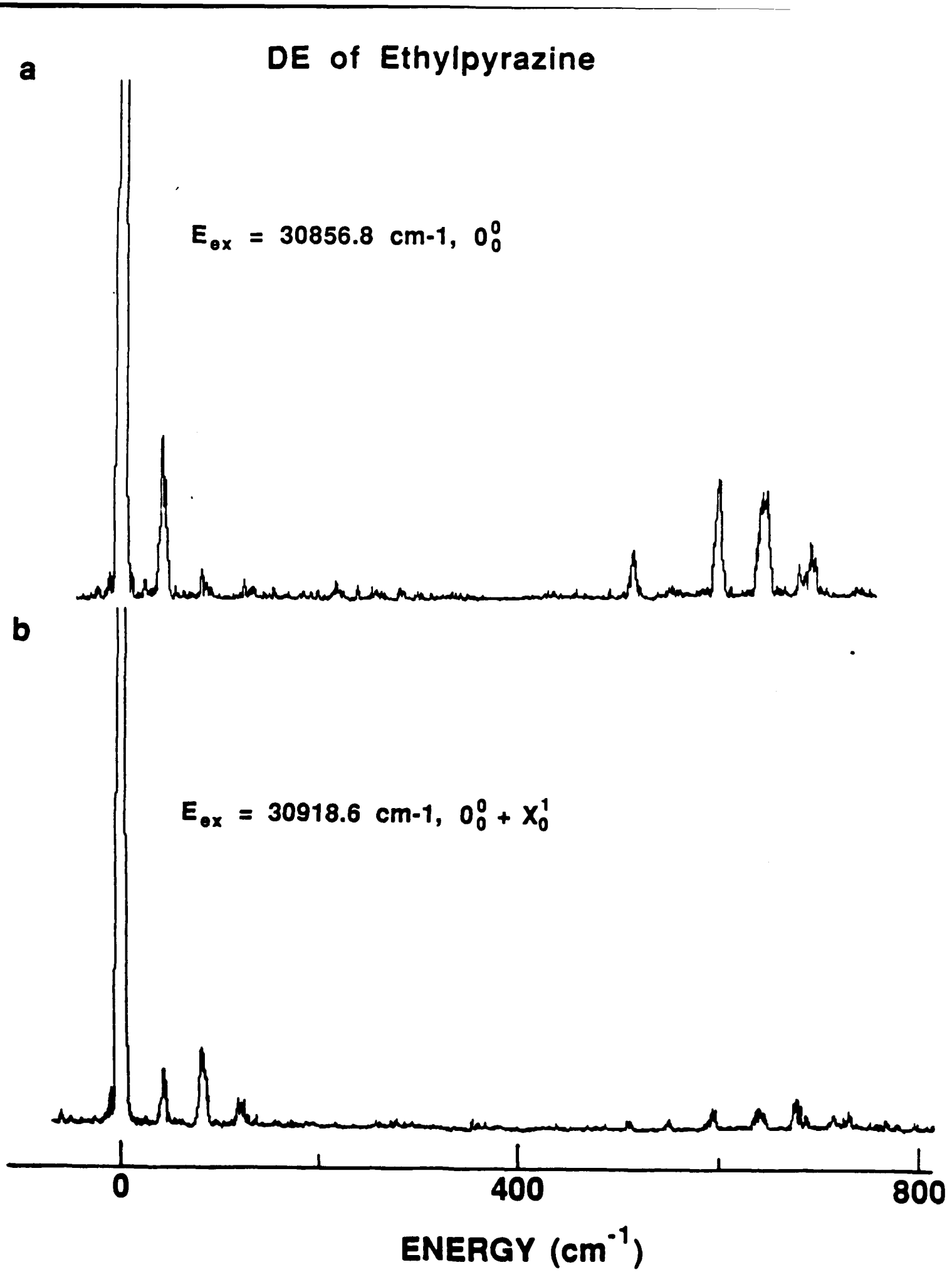
Pressure study of Methylpyrazine-h_3

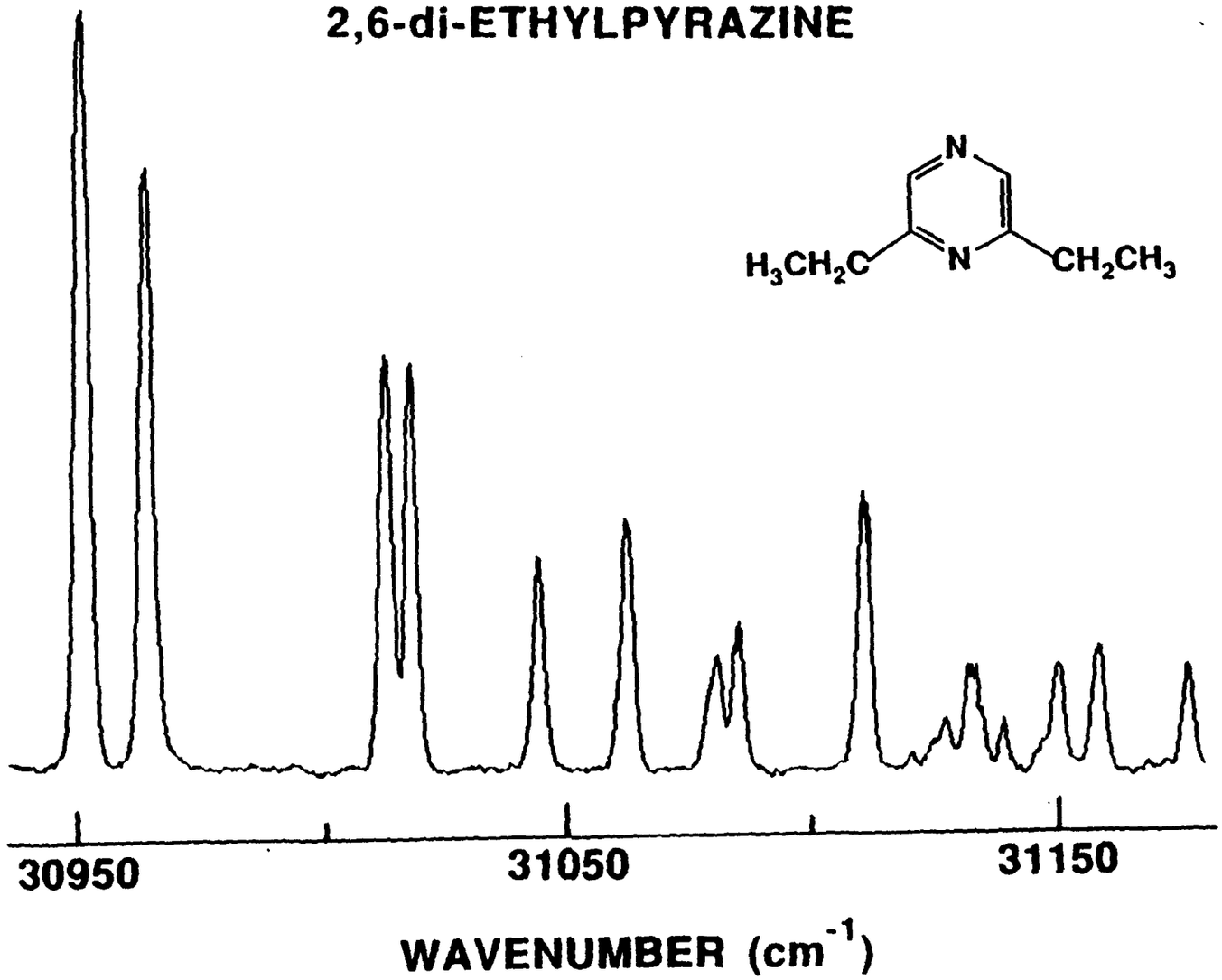


Pressure study of Methylpyrazine-d_3

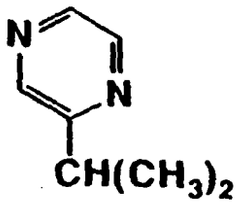



ETHYLPYRAZINE
A
B
C
D
E
F
G
N
N
CH2
CH3
30850
30950
31050
WAVENUMBER (cm-1)

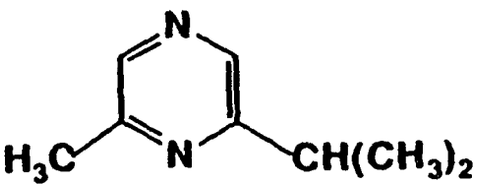

DE of Ethylpyrazine
a
E_{ex} = 30856.8 cm-1, 0_0^0
b
E_{ex} = 30918.6 cm-1, $0_0^0 + X_0^1$
0
400
800
ENERGY (cm^{-1})

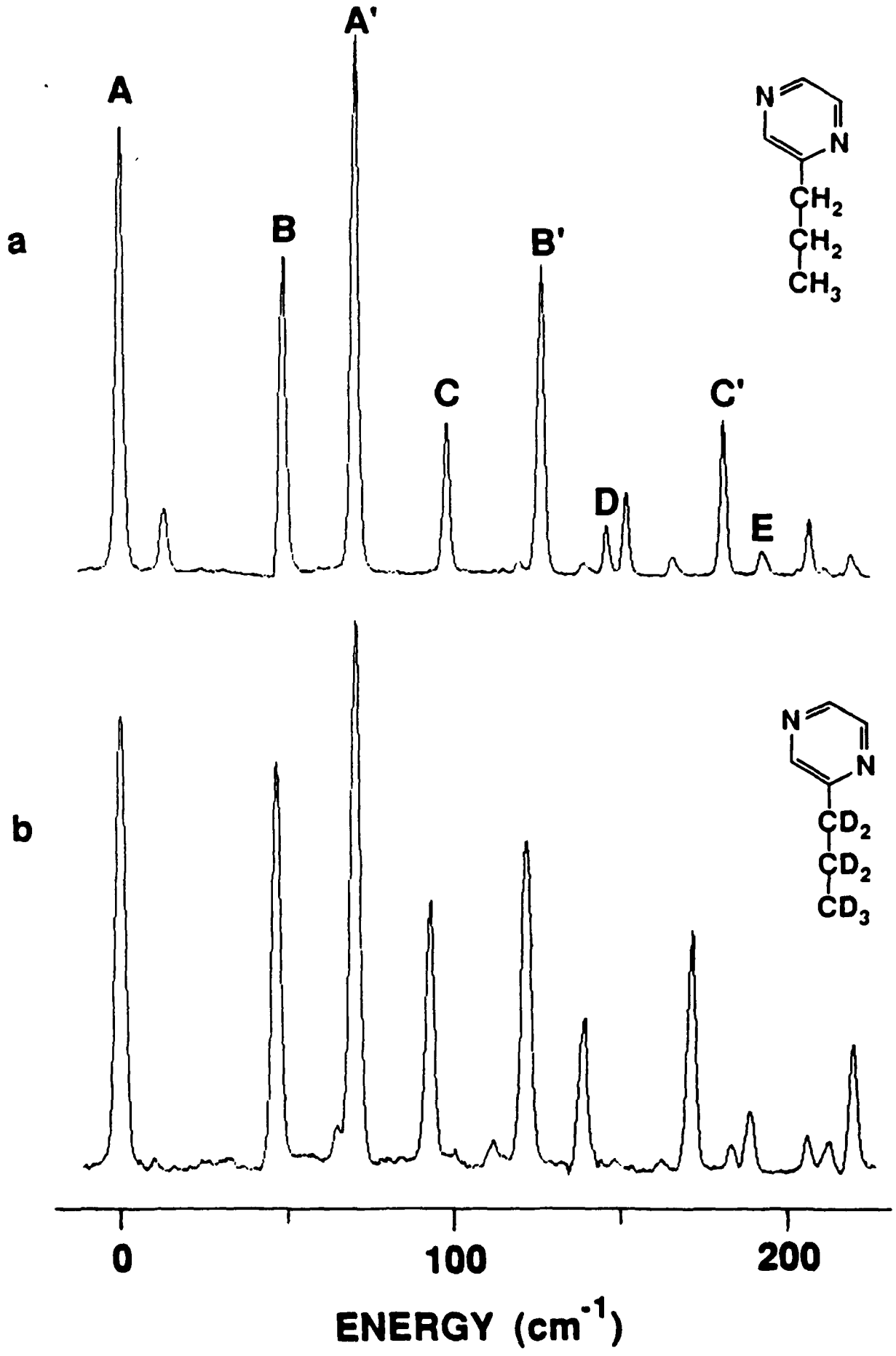

2,6-di-ETHYLPYRAZINE
N
H3CH2C
N
CH2CH3
30950
31050
31150
WAVENUMBER (cm-1)

iso-PROPYLPYRAZINE

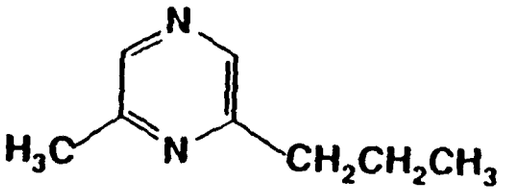


6-METHYL-iso-PROPYLPYRAZINE

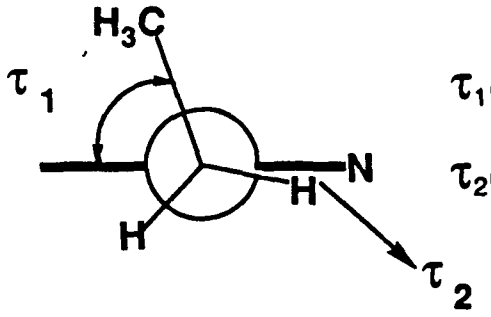



A'
A
B
B'
C
C'
D
E
a
b
N
N
CH2
CH2
CH3
CD2
CD2
CD3
0
100
200
ENERGY (cm-1)

6-Methyl-2-n-propylpyrazine



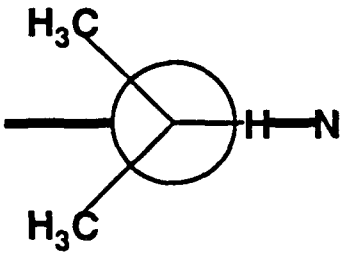
a. Ethylpyrazine - anti-gauche



$\tau_1(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta})=72^0$

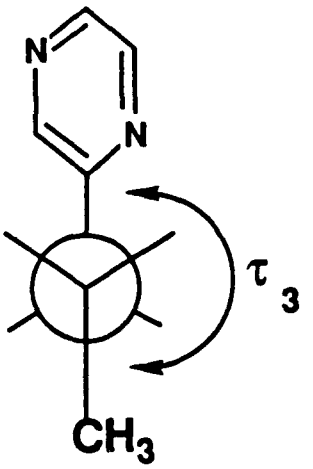
$\tau_2(N\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}H_{\alpha})=12^0$

b. iso-Propylpyrazine



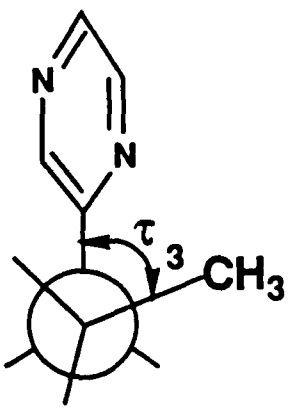
$\tau_2(N\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}H_{\alpha})=0^0$

c. n-Propylpyrazine - anti(I) and syn-gauche(II)



$\tau_1(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta})=77^0$
$\tau_2(N\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}H_{\alpha})=17^0$
$\tau_3(C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta}\text{-}C_{\gamma})=180^0$

I



$\tau_1(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta})=69^0$
$\tau_2(N\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}H_{\alpha})=9^0$
$\tau_3(C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta}\text{-}C_{\gamma})=73^0$

II

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1