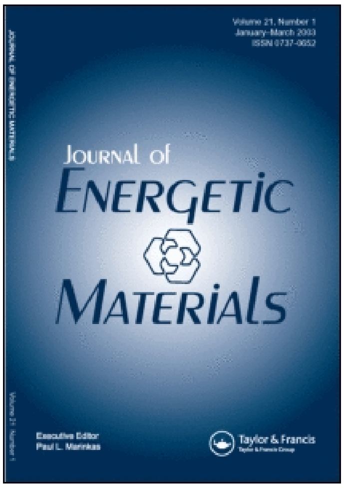

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Vibrational analysis of high-energy compounds: 1,3,3-trinitroazetidine and 1-acetyl-3, 3-dinitroazetidine

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VIBRATIONAL ANALYSIS OF HIGH-ENERGY COMPOUNDS: 1,3,3-TRINITROAZETIDINE AND 1-ACETYL-3,3-DINITROAZETIDINE

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ABSTRACT

Infrared spectra were obtained and normal coordinate calculations were made for 1,3,3-trinitroazetidine (TNAZ) and N-acetyl-3,3-dinitroazetidine (ADNAZ) in an effort to learn more about the conformational behavior of these compounds and to make assignments of the infrared bands to the appropriate normal modes of vibration. Semi-empirical molecular orbital calculations were also made in order to obtain additional information about the molecular structures. Normal coordinate calculations were made first for ADNAZ. Appropriate force constants obtained for ADNAZ were then used as starting values for TNAZ. It was shown that the observed frequency shift of the C=O stretch band of ADNAZ and the NO_2 antisymmetric stretch and NO_2 out-of-plane wag bands of the N-NO_2 group of TNAZ can be explained by a change from the conformation that is initially present to another conformation during recrystallization after mixtures are melted. However, these shifts may also be explained by intermolecular interactions that cause changes in the force constants of the bonds and angles that affect the frequencies of the three bands just mentioned.

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INTRODUCTION

1,3,3-Trinitroazetidine (TNAZ) is a novel energetic material whose properties have been under investigation for the past several years. It was first prepared in 1990 by Archibald and coworkers[1] and has become of considerable interest to the Department of Defense because it is a powerful and thermally stable, but highly volatile, energetic material. The liquid-solid phase behavior of binary mixtures of TNAZ with several other energetic compounds has been investigated,[2-5] and mixtures of additional compounds with TNAZ are currently under investigation. In particular, researchers are attempting to form binary eutectic compositions of TNAZ with other energetic materials that will result in a composite explosive of overall reduced volatility and of acceptable charge quality and performance.

It was concluded, from hot stage microscopy and differential scanning calorimetry, that TNAZ exhibits polymorphism[5] when in the form of a neat crystal or combined with some other materials. Some of those other high-energy compounds also exhibit polymorphism. One form that is stable at ambient temperature and another form that is unstable were observed for TNAZ. This behavior, or component interaction, is believed to cause the experimental eutectic phase diagrams to deviate from the calculated diagrams.

One of the binary systems whose phase diagram is being investigated at Wright Laboratory at the present time is TNAZ and N-acetyl-3,3-dinitroazetidine (ADNAZ). The experimental eutectic phase diagram of this system is one that deviates from the calculated diagram. The present paper describes work that was initiated in an effort to see if any information about the behavior of these two compounds could be explained by an in-depth study of infrared spectra of the neat compounds and of mixtures of the two. The phase diagram itself will be presented in a future paper.

Infrared vibrational spectra of mixtures of TNAZ and ADNAZ change slightly after melting and recrystallization. It is likely that each of these compounds exists as a dynamic mixture of more than one stable conformation in the liquid or solution states. Studies of the vibrational spectra of the compounds and of mixtures of the compounds may yield some information about rotational isomerism but probably not about polymorphism.

The vibrational frequencies of a compound depend on the masses of the atoms, the structure of the molecule, and the force constants for bond stretching, angle bending, and interactions between these different coordinates (stretch-stretch, stretch-bend, and bend-bend). If the structure and vibrational frequencies of a molecule are known, force constant values can usually be determined that reproduce the frequencies satisfactorily. If the force constants and frequencies are known, information about the molecular structure can often be determined. It is possible that the changes in the infrared spectra mentioned in the preceding paragraph might be explained by determining force constant values of suitable vibrational potential energy functions for TNAZ and ADNAZ and using those force constants to calculate vibrational frequencies for each compound in different stable molecular conformations. In that way, some information about the molecular conformations that exist might be obtained. Those conformations would be interchanged by internal rotation of the $O=C-CH_3$ and/or NO_2 groups in ADNAZ and of one or more of the NO_2 groups in TNAZ about the single bonds that connect the groups to the ring. In addition, normal coordinate calculations will result in descriptions of the vibrations, and the force constants can be used to interpret the vibrational spectra of similar but more complex molecules.

EXPERIMENTAL

Infrared spectra were obtained, for the crystalline compounds contained in KBr pellets, at 2 cm^{-1} resolution with a Mattson Cygnus 25 FTIR spectrometer. TNAZ was obtained from the Propulsion Division of Aerojet (Sacramento, CA) and was purified by crash-precipitation from hot ethanol solution into ice and water. HPLC analysis showed the purity to be 97.8%, with the small amounts of impurities being residual solvent and water. ADNAZ was obtained from Geo-Centers, Inc. (Lake Hopatcong, NJ). It was also purified by crash-precipitation from hot ethanol solution into ice and water, and it was dried under vacuum at 70°C. No impurities were detected by HPLC.

CALCULATIONS

Normal coordinate calculations were made with the MOLVIB program (version 6.0) written for a PC by Dr. Thomas Sundius of the University of Helsinki and distributed by Indiana University.[6] This program will handle molecules with up to thirty atoms and one hundred force constants. Semi-empirical molecular orbital calculations of molecular structures and determination of stable conformations were done with the commercially available HyperChem™ program (release 4.5).

RESULTS AND DISCUSSION

Infrared spectra that were obtained for neat ADNAZ and TNAZ are shown in Fig. 1 for the 500-2000 cm^{-1} region, and spectra for a 50:50 (mol percent) TNAZ/ADNAZ mixture before and after melting and recrystallization are shown in Fig. 2. The spectra in Fig. 1 show quite a few similarities because of the structural similarities of the two compounds, and the minor differences in the two spectra shown in Fig. 2 can also be seen.

It was decided that normal coordinate calculations should be made first for ADNAZ in an attempt to interpret the infrared vibrational spectrum of this compound, because its spectrum should be easier to interpret than that of TNAZ. The reason is that there will be more overlapping of NO_2 bands for TNAZ since there are three nitro groups. Appropriate initial force constant values were transferred from 1,3-dinitro-3-bromoazetidine, for which normal coordinate calculations had just been completed in this laboratory. The remaining force constants for ADNAZ were estimated or were transferred from an acetone force field (for the CH_3-C=O group).[7] An eighty-seven parameter modified valence force field was used, including thirty-three diagonal and fifty-four interaction force constants. Structural parameters that were used in the normal coordinate calculations were taken from an X-ray diffraction study of this molecule.[8] The conformation that was determined by X-ray diffraction to be present in the crystalline solid is shown in Fig. 3 as conformation A.

The initial CH_2 stretching and bending frequencies that were calculated for ADNAZ were quite good, and the C=O and two NO_2 antisymmetric stretches were initially calculated to be 1640, 1584, and 1604 cm^{-1} (observed: 1669, 1580, 1580 cm^{-1}). The NO_2 symmetric stretches were calculated to be 1370 and 1334 cm^{-1} (obs., 1375 and 1341 cm^{-1}). Several force constants (C-H and N-O stretches, H-C-H, N-C-H, and C-C-H bends, and appropriate interaction constants) were refined to give a least-squares fit of calculated frequencies to the observed values just given.

The methyl hydrogens were omitted in the ADNAZ calculations in order to neglect any interaction of C-C-H bending with modes of the remainder of the molecule. The force constants obtained in this way should then be more transferable to TNAZ than those that included methyl interactions. The torsions and the ring puckering mode were also omitted since their frequencies were not known. The average difference between calculated and observed wavenumbers in the zero-order run was 11.2 cm^{-1}. However, seven wavenumbers in the zero-order run had an error greater than 15 cm^{-1} each, and the maximum error was 36 cm^{-1}. Different force constants or sets of force constants were adjusted manually during the next several computer runs. Sixteen force constants were least-squares adjusted in the final run to fit twenty-seven assigned frequencies. The final average difference between observed and calculated wavenumbers was

TABLE 1. OBSERVED AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTIONS FOR ADNAZ

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contributions to the P.E.D. in terms of symmetry coordinates[b]
---	148	CNC out-of-plane bend(34),CN2 twist(19),CN2 wag(16),NO2 out-of-plane bend(13),CCN bend(12)
---	156	NCN bend(60), NO2 out-of-plane bend(20)
---	231	CNC in-plane bend(39), CO out-of-plane bend(19), CN2 rock(11)
---	254	CN2 wag(43), NO2 rock(25), CN2 twist(23)
---	301	CN2 twist(33), CCN bend(20), NO2 out-of-plane bend(19), CNC out-of-plane bend(18)
---	318	CN2 rock(38), NO2 bend(22)
---	342	CO out-of-plane bend(23),CN2 sym. stretch(14), CNC in-plane bend(10)
---	428	NO2 rock(35),NO2 bend(15),CN2 sym. stretch(15), CN2 asym. stretch(10)
465	466	NO2 bend(23),NO2 out-of-plane bend(19),CO rock (17), CN2 asym. stretch(10)
---	510	CCN bend(32), CNC out-of-plane bend(22)
515	522	NO2 rock(45), NO2 out-of-plane bend(23), CN2 twist(15)
---	552	NO2 out-of-plane bend(32),CO rock(16), NCN bend(11)
579	579	CO out-of-plane bend(50),CNC in-plane bend(36)
627	622	ring deformation(41),NO2 out-of-plane bend(31), CN2 wag(17)
---	653	NO2 bend(35), out-of-plane bend(12), CN2 rock(10)
689	685	NO2 bend(17), CN2 rock (9), CC stretch(8), CN stretch(7)
---	752	NO2 bend(30), NO2 sym. stretch(10)
855	853	CC stretch(22), CH2 wag(27), CN stretch(14)
899	893	CN2 asym. stretch(31), CH2 twist(16)
939	928	Ring deformation(30), NO2 sym. stretch(18)
972	975	CH2 wag(39), ring deformation(31), CH2 wag(15)

TABLE 1. (continued)

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contribut...ns to the P.E.D. in terms of symmetry coordinates[b]
1034	1034	CH2 twist(99)
1093	1097	CH2 rock(71)
1117	1111	CH2 rock(23), CH2 twist(23), CC stretch(14)
1150	1143	CH2 twist(34), ring deformation(27)
1194	1198	Ring deformation(61), CH2 wag(10)
1215	1221	CN stretch(22),ring deformation(20), CC stretch(13)
---	1246	CH2 rock(54), CN2 rock(12)
1304	1300	ring deformation(41), CH2 wag(15)
1341	1335	NO2 sym. stretch(51),CN2 asym. stretch(22), NO2 bend(14)
1375	1373	NO2 sym. stretch(59), CN2 sym. stretch(21)
1375	1378	ring deformation(38), CH2 wag(25)
1433	1430	CH2 bend(95)
1433	1436	CH2 bend(77)
1580	1583	NO2 asym. stretch(62), NO2 rock(19)
1580	1583	NO2 asym. stretch(78), NO2 rock(15)
1669	1669	CO stretch(74)
2963	2962	CH2 sym. stretch(99)
2963	2964	CH2 sym. stretch(99)
3013	3013	CH2 asym. stretch(99)
3013	3013	CH2 asym. stretch(99)

[a] no data were obtained below 500 cm^{-1}

[b] contributions less than 10% are omitted

a very good 3.4 cm^{-1}, and the maximum error was an acceptable 11 cm^{-1}. The observed and calculated wavenumbers and approximate potential energy distributions are given in Table 1 for ADNAZ.

All the force constants that had been determined for ADNAZ, except for those of the O=C-CH_3 group, were used in the TNAZ vibrational potential energy function to calculate the vibrational frequencies of that compound with the molecule in the conformation that had been determined by X-ray diffraction.[1] That conformer is shown in Fig. 4 as conformation A. Initial force constant values for the N-NO_2 group were taken from the C-NO_2 group. The bond lengths, bond angles, and dihedral angles that were determined by X-ray diffraction were used in the calculations. Several of the original force constants were eliminated because they had a negligible effect on the calculated frequencies, and the final potential energy function that was used consisted of seventy-three force constants, including twenty-seven diagonal and forty-six interaction constants. The average difference between calculated and observed differences in the zero-order run was 15 cm^{-1}, so changes had to be made in quite a few of the force constant values. In the second run, the C-H stretch, N-O stretch, H-C-H bend, C-H,C-H interaction, C-N,C-N interaction, and C-N,N-O interaction constants were adjusted to fit several observed frequencies. The Jacobian matrix elements and potential energy distributions were used in all force constant adjustments to determine which force constants to adjust. Over the next several runs, different force constants or sets of force constants were adjusted manually to better fit the frequencies above 900 cm^{-1}. Fourteen force constants were then adjusted with the least-squares program to better fit those frequencies above 900 cm^{-1}, with the average error being 4.8 cm^{-1}. Several runs were then made, with different sets of force constants being adjusted manually, in an effort to fit the frequencies below 900 cm^{-1}. In the final run, twenty force constants (eight diagonal and twelve interaction) were adjusted by the least-squares program to fit twenty-four assigned frequencies. The average difference between calculated and observed values was 1.3 cm^{-1}. The observed and calculated wavenumbers and the band assignments in terms of approximate potential energy distributions are given in Table 2.

There were no FTIR frequency data obtained for the region below 500 cm^{-1}.

Table 3 lists the infrared bands observed for TNAZ that are not overlapped by ADNAZ bands, and vice versa, for the neat compounds and for a 50:50 (mol percent) mixture of TNAZ and ADNAZ before and after melting and recrystallization. It can be seen that the carbonyl stretch band at 1669 cm^{-1} for neat ADNAZ shifts downward to 1657 cm^{-1} in the melt. It was thought that an explanation for this shift might be a change in structure from the X-ray structure (Fig. 3 - conformation A) to some other structure, such as conformation B in Fig. 3. This difference in structure results from internal rotation about the N-C bond between the ring nitrogen and the acetyl carbon. In order to determine the dependence of C=O stretching frequency on structure, the vibrational frequencies of structure B were calculated with the force constants that were determined for structure A. The C=O stretching frequency for B was calculated to be 1646 cm^{-1}, which is a downward shift from the value of 1669 cm^{-1} in A, in agreement with the observed trend. None of the other bands for ADNAZ are expected to be more than 2 or 3 cm^{-1} different in structures A and B, and this is what is observed. The HyperChem™ program was used to do a conformational search on the ADNAZ molecule at the AM1 level. It was found that both conformations shown in Fig. 3 are stable and therefore should exist in appreciable amounts. Conformation A was calculated to be approximately 400 cal/mole more stable than B.

Table 3 also shows that the 1537-cm^{-1} TNAZ band (NO_2 antisymmetric stretch of the N-NO_2 group) shifts upward to 1553 cm^{-1} in the 1:1 melt. This is the opposite direction of the shift of the C=O stretch band in ADNAZ. There is also a downward shift of the band observed at 665 cm^{-1} in neat TNAZ to 650 cm^{-1} in the melt. This band should be due to the NO_2 out-of-plane bend of the N-NO_2 group. In an effort to explain the frequency shift of the two bands just mentioned, additional normal coordinate calculations were made for TNAZ, assuming that the molecule exists in the conformation shown as conformation B in Fig. 4. A conformational search with the HyperChem™ program shows that both of these conformations, which are

TABLE 2. OBSERVED AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTIONS FOR TNAZ

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contributions to the P.E.D. in terms of symmetry coordinates[b]
---	148	CNN bend(44),CN2 wag(19),CN2 twist(19),NO2 rock(16)
---	159	CN2 bend(44),NO2 out-of-plane bend(27),NO2 rock(11)
---	240	CNN bend(28), CN2 rock(20)
---	242	CN2 wag(36),NO2 out-of-plane bend(27),CN2 twist(18)
---	303	CN2 twist(28), NO2 rock(29), CNN bend(24)
---	339	CN2 rock(42)
---	362	CNN bend(22) NO2 out-of-plane bend(18), NCN sym. stretch(17),
---	416	NO2 rock(41), ONO bend(13), NCN stretch(23)
---	507	NO2 out-of-plane bend(23),NN stretch(21), NCN stretch(11),ONO bend(22)
517	517	NO2 rock(64), NO2 out-of-plane bend (12)
544	544	NO2 out-of-plane bend(25),NO2 rock(21),CNN bend(14), CN2 twist(13)
604	604	NO2 out-of-plane bend (37), ONO bend(14)
---	654	NO2 out-of-plane bend (31),CN2 wag(29),NO2 rock(14)
665	661	NO2 out-of-plane bend (67),CNN bend(11),CNN bend(11)
714	713	ONO bend(33), CN2 rock(20), NO2 sym. stretch(12)
762	762	ONO bend(42), NO2 sym. stretch(20)
843	836	ONO bend(27), NO2 sym. stretch(21), CH2 wag(12), ring deformation(16)
---	890	ring deformation(29), NO2 sym. stretch(11)
908	911	NCN stretch(25), NO2 sym. stretch(20), CH2 twist(15)
---	968	CH2 wag(32), NN stretch(17), NO2 sym. stretch(14), ring deformation(23)
---	1004	ring deformation(82)
1061	1061	CH2 twist(88)
1086	1085	CH2 wag(36), ring deformation(21), CH2 rock(10)
1113	1113	CH2 rock(75)
---	1164	CH2 twist(56), CH2 rock(12), ring deformation(10)

TABLE 2. (continued)

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contributions to the P.E.D. in terms of symmetry coordinates[b]
1182	1178	ring deformation(32),CH2 twist(15),NO2 sym. stretch(12)
1219	1222	CH2 wag(61), CN2 wag(11)
---	1242	CH2 rock(29), ring deformation(14), CH2 wag(13)
---	1264	NO2 sym. stretch(19), CH2 wag(18), ring deformation(16), CH2 rock(13)
1279	1281	NO2 sym. stretch(33), NN stretch(21), ONO bend(21)
1339	1339	NO2 sym. stretch(35), NCN asym. stretch(27), ONO bend(17)
1367	1367	NO2 sym. stretch(45), ONO bend(21), NCN sym. stretch(20)
---	1397	CH2 bend(85)
1428	1428	CH2 bend(59), CH2 wag(13), ring deformation(11)
1538	1537	NO2 asym. stretch(76), NO2 rock(16)
1589	1589	NO2 asym. stretch(86), NO2 rock(11)
1589	1589	NO2 asym. stretch(72), NO2 rock(16)
2969	2969	CH2 sym. stretch(100)
2976	2976	CH2 sym. stretch(100)
3022	3022	CH2 asym. stretch(99)
3037	3037	CH2 asym. stretch(99)

[a] no data were obtained below 500 cm^{-1}

[b] contributions less than 10% are omitted

interconvertible, should be stable. According to the AM1 calculations, conformation A of TNAZ is more stable than B by less than 100 cal/mole. However, it should be pointed out that the AM1 calculations are for the gaseous state and the results are not applicable to these crystalline substances.

TABLE 3. OBSERVED VIBRATIONAL WAVENUMBERS (CM^{-1}) FOR TNAZ (NEAT), ADNAZ (NEAT), AND A 1:1 MIXTURE OF TNAZ AND ADNAZ (INITIAL MIXTURE AND MELT)

TNAZ	ADNAZ	MAJOR P.E.D. CONTRIBUTOR	1:1 GROUND	1:1 MELT
n.b.	1669	C=O stretch	1669	1657
1537	n.b.	NO_2 asym str	1541	1553
n.b.	1304	ring def	1304	1304
1279	n.b.	NO_2 sym str	1281	1281
n.b.	1034	CH_2 twist	1034	1036
n.b.	972	CH_2 wag	972	976
762	n.b.	NO_2 def	762	762
n.b.	689	NO_2 def	689	686
665	n.b.	NO_2 o-p	666	650
n.b.	579	C=O o-p	579	581
n.b.	465	NO_2 def	465	465

n.b. = no band observed

The force constants that provided the fit shown in Table 2 for conformation A were used to calculate the vibrational frequencies of conformation B. The N=O stretch and out-of-plane bending wavenumbers were calculated to be 1525 and 694 cm^{-1}, respectively, both of which are shifted from the conformation A values in the direction opposite to that which is observed. Therefore, it was assumed that conformation B is the one that gave rise to the bands listed for TNAZ in Table 3, and the force constants were adjusted to fit the calculated wavenumbers of conformation B to the observed values. This means that the 1537 and 665 cm^{-1} bands were assigned to B rather than to A. The force constants that were determined in this way for conformation B were then used to calculate the frequencies of conformation A. The (N)-NO_2 stretch and (N)-NO_2 out-of-plane bend wavenumbers were calculated to be 1550 and 647 cm^{-1} for conformation A, which are in good agreement with the observed values in Table 3. The other bands listed in Table 3 that are due only to TNAZ (1279 and 762 cm^{-1}) do not shift in the melt, in agreement with the calculations. The frequency shifts of the TNAZ bands at 1537 and 665 cm^{-1} are also observed in the TNAZ/N-nitroso-3,3-dinitroazetidine system.[9] That is, these bands are again shifted to 1553 and 650 cm^{-1} in the mixtures that were recrystallized after melting. Observations of rotational isomerism involving $C(NO_2)_2$ groups have been made previously. In fact, polymorphism in 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) was explained by the existence of at least two conformers in the $>C(NO_2)_2$ fragment of solid DNNC, each with exaggerated atomic oscillations.[10] Therefore, it is possible that the polymorphism in ADNAZ and/or TNAZ could be caused by the existence of more than one conformation. The infrared studies on DNNC suggest that C-H···O hydrogen bonding is relatively unimportant in that compound,[10] and it does not seem likely to be the cause of the observations reported in this paper.

Infrared spectra were also obtained for a 97.5%/2.5% TNAZ/ADNAZ mixture before and after melting and recrystallization. The NO_2 antisymmetric stretch band and the NO_2 out-of-plane wag band of the N-NO_2 group do not shift at all, as they did in the 50/50 mixture. This suggests that simply melting TNAZ and letting it recrystallize does not induce a conformational change. If such a change does indeed occur, the presence of a second component is required for interaction with the TNAZ. It was concluded during the TNAZ/TNT work that the thermal characteristics associated with that system were affected by component interaction.[11] That may also be the case with the TNAZ/ADNAZ system. If significant amounts of both components are present, their intermolecular interactions may either (1) cause a change in conformation, or (2) cause a change in the force constants that affect the frequencies of the antisymmetric stretch and out-of-plane wag of the N-NO_2 group. There would be insufficient ADNAZ in the 97.5/2.5 mixture to see this effect. There are no ADNAZ bands intense enough to be observed in the IR spectrum at this low concentration. If the intermolecular interaction affects only the N=O bond and NO_2 out-of-plane bend force constants of TNAZ, the N=O bond force constant would have to increase from 7.63 to 7.81 mdyne/Å and the out-of-plane bend force constant would have to decrease from 0.360 to 0.352 mdyne·Å/(rad)^2. (These are, of course, values that were required, in combination with other force constants, to reproduce the frequencies of interest, and their absolute values are not the actual force constant values of the coordinates involved.) In order to save space, the list of force constants will not be given here, but they are available from the authors.

It should be pointed out that Tables 1 and 2 contain several calculated wavenumbers to which observed values are not assigned. This is the normal situation for molecules with as many atoms as these molecules have, because some vibrational modes usually have intensities that are too low to be observed. Infrared intensities were calculated with the HyperChem™ program, which indicated that several bands should be unobserved because of low intensity. Raman spectra would provide additional observed values, especially in the region below 500 cm^{-1} where no infrared spectra were obtained, but no Raman spectrometer is available.

CONCLUSIONS

The normal coordinate calculations discussed in this paper provide one possible explanation of the behavior of the TNAZ/ADNAZ system. Each of the two neat compounds could be in one conformation, which changes to another conformation during recrystallization after being melted together. This could be partially due to low barriers of internal rotation of the NO_2 and $O=C-CH_3$ groups, which could make many conformations possible. This could also be the explanation of the existence of polymorphism in one or both of these compounds. It has been shown that nitromethane[12] and nitroethane[13] have very low barriers to internal rotation of the NO_2 group. The calculations also resulted in vibrational assignments and modified valence force fields that can be used to calculate fundamental vibrational frequencies of more complex molecules that contain the ring$<(NO_2)_2$ group. Another possible explanation of the frequency shifts described in this paper is a change in the force constants of the C=O bond of ADNAZ and the N=O bond and angles that comprise the out-of-plane wag of the $N-NO_2$ group of TNAZ. These minor changes in force constant values could be caused by intermolecular interactions between the ADNAZ and TNAZ molecules.

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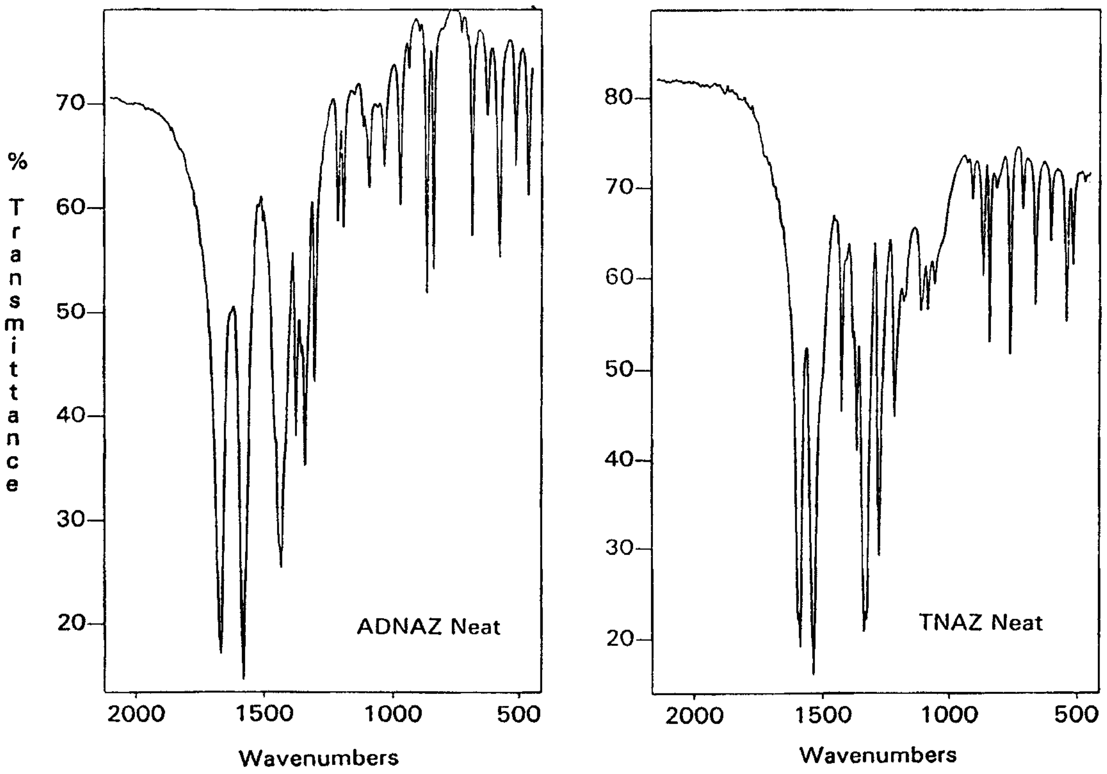

FIGURE 1

Infrared spectra for ADNAZ and TNAZ in KBr pellets

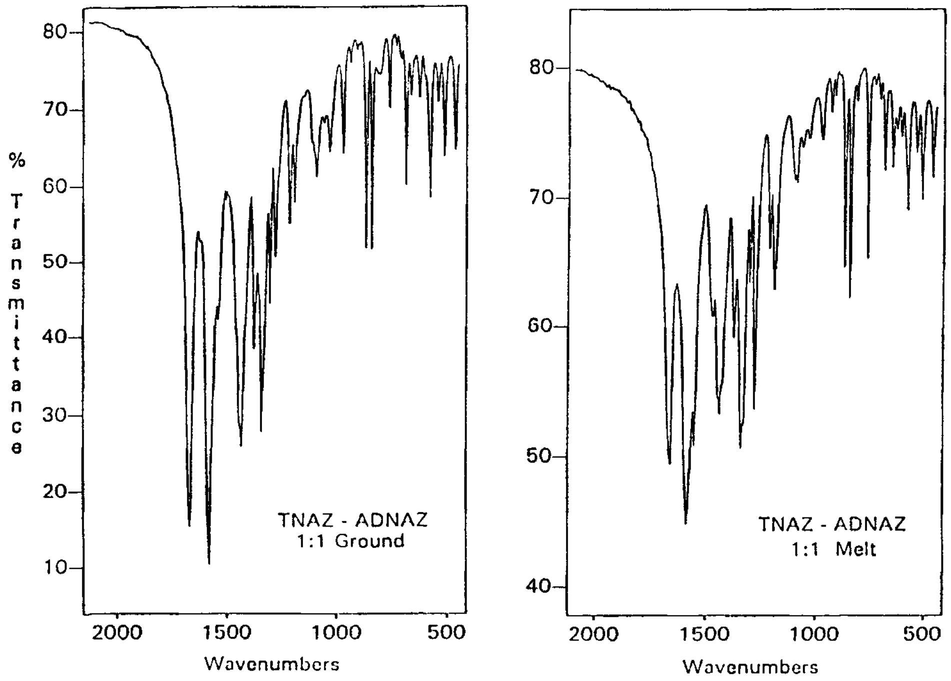

FIGURE 2

Infrared spectra for a 50:50 mixture (mol percent) of TNAZ and ADNAZ. Left, initial mixture; Right, same mixture after melting and recrystallization

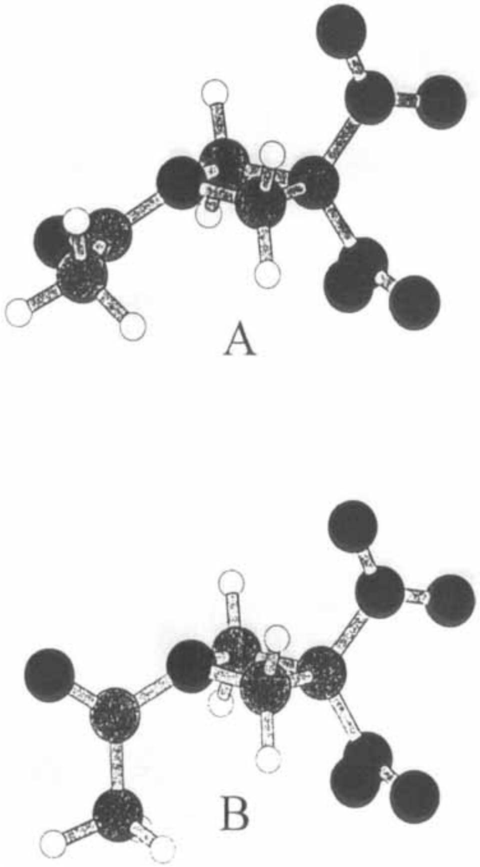

FIGURE 3

Conformations of ADNAZ. Conformation A, structure as determined by X-ray diffraction; conformation B, same as A, but with the $O=C-CH_3$ group rotated 90° about the N-C bond

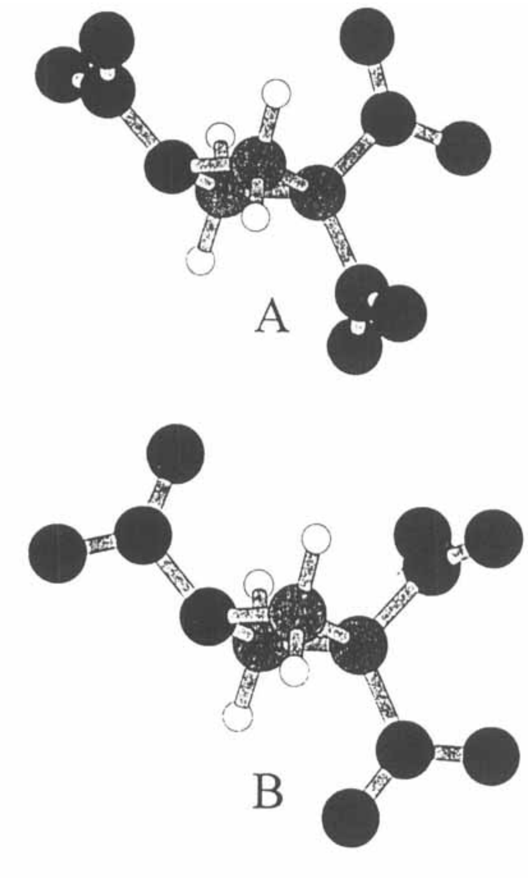

FIGURE 4

Conformations of TNAZ for which calculations were done. Conformation A; conformation as determined by X-ray diffraction; Conformation B; same as A, but with NO_2 groups rotated about the C-N or N-N bond by 90°