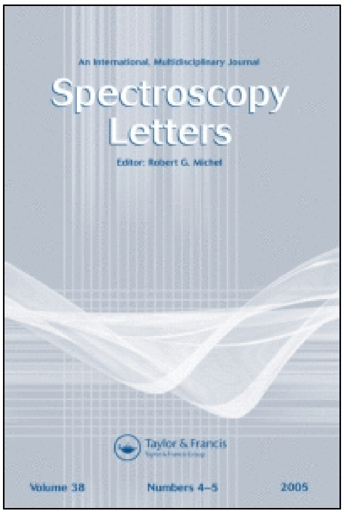

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Normal Coordinate Analysis of 3-Bromo-1,3-Dinitroazetidine

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NORMAL COORDINATE ANALYSIS OF 3-BROMO-1,3-DINITROAZETIDINE

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ABSTRACT

The infrared spectrum of 3-bromo-1,3-dinitroazetidine was interpreted with the aid of normal coordinate calculations. A seventy-two parameter modified valence field was used in those calculations, and the observed

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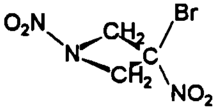
wavenumbers were fit with an average error of 2.5 cm^{-1}. An assignment of the bands in terms of symmetry coordinates is given. Many of the force constants were transferred to 1-acetyl-3,3-dinitroazetidine to aid in normal coordinate calculations for that compound.

INTRODUCTION

The experimental phase diagrams of the TNAZ/ADNAZ (1,3,3-trinitroazetidine/1-acetyl-3,3-dinitroazetidine) and the TNAZ/ NO-DNAZ (1-nitroso-3,3-dinitroazetidine) systems deviate from the calculated diagrams,[1] perhaps because of the presence of polymorphism in one or more of these compounds. The infrared vibrational spectra of mixtures of ADNAZ and TNAZ and of TNAZ and NO-DNAZ change slightly after melting and recrystallization, so an explanation of the phase behavior might be obtained from an in-depth study of the infrared spectra. The real question was whether the behavior was the result of polymorphism or some other type of behavior such as a change in structure due to rotational isomerism. It is likely that each of these compounds exists as a dynamic mixture of more than one stable conformation in the liquid state or in solution.

It was thought that studies of the vibrational spectra of ADNAZ and TNAZ may yield some information about rotational isomerism but probably not about polymorphism. The changes in the infrared spectra 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 molecular conformations. In that way, some information about the molecular conformations that exist might be obtained, if rotational isomerism does occur. Those conformations would be interchanged by internal rotation of the O=C-CH_3 and/or NO_2 groups about the C-N bonds in ADNAZ and of one or more of the NO_2 groups in TNAZ about the N-N and C-N bonds. Initial values of the force constants were not available for most of the force constants, so normal coordinate calculations were made first for the slightly less complex molecule 1,3-dinitro-3-bromoazetidine (hereafter called Br-DNAZ) in order to obtain force constants to transfer to ADNAZ. It should be easier to make a vibrational assignment with the aid of the normal coordinate calculations for Br-DNAZ than for ADNAZ. Appropriate force constants values determined for ADNAZ would then be used as starting values for TNAZ. The work on Br-DNAZ is described in the current paper. The ADNAZ and TNAZ work has also been



Br-DNAZ

completed, and a paper describing the vibrational analyses of those two compounds has been written.[2]

EXPERIMENTAL

The IR spectrum of Br-DNAZ (KBr pellet) was supplied by M. Hiskey of Los Alamos National Laboratory. The spectrum was obtained at 2 cm^{-1} resolution with a Bio-Rad FTS-40 spectrometer.

CALCULATIONS

Normal coordinate calculations were done with the program MOLVIB (version 6.0), which was developed by Dr. Thomas Sundius of the University of Helsinki. The program is distributed by the Quantum Chemistry Program Exchange of Indiana University.[3] The program will handle up to thirty atoms and one hundred force constants. The molecular parameters that were used were determined with the commercial HyperChem™ program. That list of parameters is not given here, but it is available from the authors.

RESULTS AND DISCUSSION

Unfortunately, not much force constant value information was available for the moities involved, so an educated guess at most of the values had to made.

Initial C-NO_2 constants were taken from C_2H_5-NO_2[4] and some of the ring force constants were taken from cyclobutane.[5] The calculated C-H stretching frequencies were very good, but the NO_2 stretches were in error by a significant amount [calc., 1624, 1619, 1464, 1364 cm^{-1}; obs., 1561, 1529, 1330, 1260 cm^{-1}]. Several runs were made, with the force constants that have the largest effect on the NO_2 stretching frequencies being manually adjusted. These were the NO stretch, NO-NO interaction, NNO and CNO bends, and NNO-NNO and CNO-CNO interactions. In addition, the CCH and NCH bends and CCH-CCH and CCH-NCH interactions affected the NO_2 symmetric stretches because of the mixing of normal coordinates. The Jacobian matrix and potential energy distributions were used as guides to determining which force constants needed to be adjusted.

The infrared spectrum for a crystalline sample of 1,3-dinitro-3-bromoazetidine in a KBr pellet was obtained from Los Alamos National Laboratory.[6] The structural parameters (bond lengths, bond angles, torsional angles) were obtained by doing semi-empirical molecular orbital calculations with a MNDO-AM1 force field. The HyperChem™ program was used for those calculations. A seventy-two parameter modified valence force field (vibrational potential energy function), which included twenty-six diagonal and forty-six interaction force constants, was used for a molecule of Br-DNAZ that has the two nitro groups on opposite sides of the cyclic plane. The NO_2 torsions and the ring puckering mode were neglected.

Normal coordinate calculations were completed satisfactorily for 1,3-dinitro-3-bromoazetidine. Thirty-three computer runs were made, with different sets of force constants being manually adjusted to improve the fit between observed and calculated vibrational wavenumbers. In the final run, the least-squares part of the computer program was allowed to adjust 21 force constants to fit 26 observed wavenumbers. The average difference between observed and calculated values was 2.5 cm^{-1}. The observed and calculated wavenumbers and the approximate potential energy distributions in terms of symmetry coordinates are given in Table 1. An X-ray diffraction structure was not available for this compound, so it is not known if the two nitro groups are on opposite sides of the cyclic plane (called isomer A in what follows) or on the same side of that plane (called isomer B). (The cyclic 'plane' may actually be puckered slightly.) Therefore, the structure of B was calculated (AM1), and the force constants that were obtained for A were used to calculate the vibrational frequencies of B. Comparison of the calculated vibrational frequencies of

TABLE 1. OBSERVED AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTIONS FOR 1,3-DINITRO-3-BROMOAZETIDINE

Obs.[a] cm^{-1}	Calc. cm^{-1}	Main % contributions to the P.E.D. in symmetry coordinates (contributions less than 10% are omitted)
---	135	CNBr twist(23), CNN bend(42), CNBr rock(19), NO2 rock(16)
---	170	NCBr bend(47), NO2 out-of-plane bend (34)
---	218	CNBr rock(50), CNBr twist(38)
---	252	CNN bend(28), CN6 stretch(19), NO2 out-of-plane bend (9)
---	279	NO2 rock(33), CNN bend(30), CNBr twist(26)
---	281	CBr stretch(64)
---	364	NO2 out-of-plane bend(35), CNN bend(24), CN stretch(15)
---	472	NO2 rock(63), CC2 asym. stretch(11)
511	501	NO2 out-of-plane bend(28), NO2 bend(20), CBr stretch(16), NN stretch (15)
536	538	NO2 rock(43), CNBr rock(14), CNN bend(24)
611	613	NO2 out-of-plane bend(41), NO2 bend(31)
642	644	NO2 out-of-plane bend(52), CNN bend(28)
---	681	NO2 bend(56)
761	764	NO2 bend(25), NO2 out-of-plane bend(13)
809	814	NN stretch (18), CC2 sym. stretch(15), NC2 sym. stretch(10)
847	846	CC2 asym. stretch(44), CH2 wag(44)
904	903	CN stretch(18), NO2 sym. stretch(11), CH2 rock(20), CH2 twist(16)
935	936	CH2 wag(47), NN stretch (13), CC2 sym. stretch(13)
1025	1022	CH2 twist(86), CH2 rock(12)
1055	1056	CH2 rock(83), CH2 twist(12)
1098	1101	CH2 twist(48), CH2 rock(18), NC2 sym. stretch(13)
---	1138	NC2 asym. stretch(73)
1160	1158	CH2 wag(22), NC2 sym. stretch(21), CC2 sym. stretch(17), CH2 twist(12)

(continued)

TABLE 1 (Continued)

Obs.[a] cm^{-1}	Calc. cm^{-1}	Main contributions to the P.E.D. in symmetry coordinates (%) (contributions less than 10% are omitted)
1180	1181	CH2 wag(43), CC2 asym. stretch(31)
1260	1258	NO2 sym. stretch(50), CH2 rock(24), NO2 bend(11)
1276	1275	CC2 sym. stretch(28), NC2 sym. stretch(21), NO2 sym. stretch(13)
1330	1331	NO2 sym. stretch(48), NN stretch (26), NO2 bend(12)
1347	1347	CN stretch(35), NO2 sym. stretch(25), CH2 rock(16), NO2 bend(11)
1443	1435	CH2 bend(95)
1443	1452	CH2 bend(83)
1529	1530	NO2 asym. stretch(84), NO2 rock(12)
1561	1560	NO2 asym. stretch(84), NO2 rock(10)
2967	2965	CH2 sym. stretch(99)
2967	2968	CH2 sym. stretch(99)
3026	3024	CH2 asym. stretch(99)
3026	3026	CH2 asym. stretch(99)

[a] No data available below 500 cm^{-1}

these two isomers indicates that the frequencies of the two should be indistinguishable. This is probably because the nitro group bonded to the ring nitrogen is too far from the two groups (bromine and nitro) bonded to the carbon for them to interact with each other. The heat of formation of isomer A was calculated to be 64 Kcal/mole with AM1 but only 22 Kcal/mole with PM3. The heat of formation of isomer B was calculated to be 64 (AM1) or 23 (PM3) Kcal/mole.

Table 1 shows the value calculated at 281 cm^{-1} to be mainly C-Br stretch, whereas the C-Br stretch band for this molecule should be in the 500-600 cm^{-1} region. It is not uncommon for the potential energy distribution to show this 'anomaly'. For example, the tertiary "C-Br stretch" in 3-bromo-3-methylpentane was observed at 574 cm^{-1}, but the 292 cm^{-1} band (calc., 288 cm^{-1}) had the largest calculated C-Br stretch contribution. The C-Br stretching force constant used in the present case (2.7 mdyne/Å) is actually larger than the normal hydrocarbon value (2.31-2.32 mdyne/Å)[7-9].

Finally, the IR spectrum of the analogous chlorine compound, Cl-DNAZ, is available,[6] and the Br-DNAZ force constants should be useful in normal coordinate calculations for that compound.

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