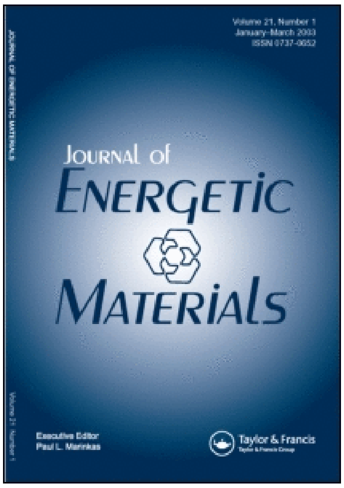

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Vibrational analysis of high-energy compounds: 1-nitroso-3,3-dinitroazetidine

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1-NITROSO-3,3-DINITROAZETIDINE

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ABSTRACT

Infrared spectra were obtained and normal coordinate calculations were made for 1-nitroso-3,3-dinitroazetidine (NO-DNAZ) in order to make assignments of the infrared bands to the appropriate normal modes of vibration. Only one stable conformation was found by semi-empirical molecular orbital calculations. Appropriate force constants that had been obtained for TNAZ were used as starting values for NO-DNAZ. The transferability of the force constants was quite good, so they should be useful in calculations for other dinitroazetidines. Force constant refinements resulted in calculated vibrational wavenumbers that differed from observed values by an average of only 1.9 cm^{-1}.

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INTRODUCTION

Infrared spectra were recently obtained for the two high-energy compounds 1,3,3-trinitroazetidine (TNAZ) and N-acetyl-3,3-dinitroazetidine (ADNAZ).[1] Those spectra were interpreted with the aid of normal coordinate calculations, and it was concluded that more than one stable conformation of each compound may exist. If this is so, the conformations would differ by the torsional angles that the external groups make with the ring. TNAZ and ADNAZ form a binary eutectic system whose phase diagram has been investigated in this laboratory.[2] Several other binary systems in which TNAZ is combined with other high-energy compounds have also been investigated,[3-6] and others are currently being studied. One of the binary systems now being studied is TNAZ and 1-nitroso-3,3-dinitroazetidine (NO-DNAZ). FTIR spectra have now been obtained and normal coordinate and molecular structure calculations have been made for NO-DNAZ in order to make a vibrational assignment and perhaps learn something about its conformational behavior.

Vibrational assignments are often supported by normal coordinate calculations. More confidence is placed in the force field and in the vibrational assignment if the resulting force constants can be successfully transferred to other compounds in the same family. If the assignments of the observed bands to fundamentals and combinations or overtones is not in doubt, the force constant values that give a good frequency fit can be used to obtain reasonable potential energy distributions. However, for assignments that are in doubt, normal coordinate calculations may not help in determining the correct assignment. Since the TNAZ and NO-DNAZ molecules differ only in the group bonded to the ring nitrogen, most of the force constants of NO-DNAZ should be nearly the same as those of TNAZ. The TNAZ force constant values will therefore be transferred to NO-DNAZ in order to check their transferability. The availability of these force constant values should simplify the normal coordinate calculations for NO-DNAZ.

EXPERIMENTAL

Infrared spectra were obtained, for the solid compound contained in a KBr pellet, at 2 cm^{-1} resolution with a Mattson Cygnus 25 FTIR spectrometer. NO-DNAZ was obtained from Los Alamos National Laboratory. The sample had a purity greater than 99%, as determined by NMR spectrometry, and it was used without further purification.

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.[7] This is a program for the calculation of harmonic force fields and vibrational modes of molecules with up to thirty atoms and one hundred force constants. Molecular mechanics and semi-empirical molecular orbital calculations of molecular structures and determination of stable conformations were done with the commercially available HyperChem™ program (release 4.5).

As stated previously, IR spectra were determined for the solid state, and therefore solid-state wavenumbers were used in the normal coordinate calculations. Some of the vibrational wavenumbers will be slightly different from gas-phase values because of intermolecular interactions and crystal effects in the solid. However, this has little consequence on the calculations because the force constants are only approximate since the vibrations are assumed to be harmonic.

RESULTS AND DISCUSSION

The infrared spectrum that was obtained for NO-DNAZ is shown in Fig. 1 for the region above 500 cm^{-1}. The two NO_2 antisymmetric stretching frequencies obviously overlap, giving rise to the most intense band in the spectrum at 1573 cm^{-1}. The next most intense band, at 1333 cm^{-1}, must be due to overlapping NO_2 symmetric stretches. The normal region for the N=O stretch of a nitrosoamine ($R_2N-N=O$) is ca. 1450 cm^{-1} for the compound in solution or 1490 cm^{-1} for the vapor.[8] The phase difference can certainly affect the frequency, but the nearest band to these regions for NO-DNAZ (KBr Pellet) is a medium intensity band that was observed at 1421 cm^{-1}, so this band must be due to that mode. Since one of the two CH_2 bending bands should also be observed in this region, it is assumed that a CH_2 bend overlaps the nitroso stretch at 1421 cm^{-1}. Most of the other bands will involve considerable mixing of normal modes, so calculations must be done to describe the motions responsible for those bands.

The structure of crystalline NO-DNAZ has been determined by X-ray diffraction.[9] The nitroso nitrogen is bent out of the CNC plane by only 11.4°,[9] whereas the N-N bond in TNAZ was bent out of the plane by 39.6°.[10] The structural parameters that were used in the normal coordinate calculations were taken from the X-ray structure.[9] A ball-and-stick model of that structure is shown in Fig. 2.

A sixty-four parameter modified valence force field (vibrational potential energy function) was used for NO-DNAZ, which included twenty-four diagonal and forty interaction force constants. The torsions and ring puckering modes were omitted because their frequencies are unknown. Initial values of all force constants were taken from the TNAZ force field.[1] The N-N and nitroso N=O stretching constants were assumed to be larger than for TNAZ, and were therefore set a little higher than the TNAZ values. The N-N bond length in NO-DNAZ is shorter than in TNAZ (1.292 vs 1.351 Å), which indicates more double-bond character to this bond in NO-DNAZ and therefore a larger force constant. In addition, the N-O bonds in a nitro group are equivalent, and the resonance structure must therefore be intermediate between a double and single bond. There will be less resonance between N-N and N-O in NO-DNAZ than between the two N-O bonds in a nitro group, so the nitroso N-O will have more double-bond character than for nitro, and the nitroso N-O force constant must be larger than that of the nitro N-O.[11] The nitroso

N-O force constant in NO-DNAZ was adjusted to 7.99 mdyn/Å, whereas in TNAZ, the N-O force constant of the N-NO_2 group was 7.63 mdyn/Å. Even so, the NO_2 antisymmetric stretching frequency in TNAZ is higher than the nitroso N-O stretch because of the stretch-stretch interaction between the two N-O bonds that give rise to an antisymmetric stretch and a symmetric stretch.

The transferred force constants resulted in calculated wavenumbers in the zero-order run that were quite good, with the average difference between calculated and observed values being 10.6 cm^{-1} for twenty-one assigned wavenumbers. Only one calculated value (895 cm^{-1}) differed more than a reasonable amount from the observed value (855 cm^{-1}). This may indicate that the analogous band for TNAZ had been assigned incorrectly.

The Jacobian matrix and potential energy distributions were used as indicators of the force constants that needed to be adjusted to obtain a better fit of calculated to observed wavenumbers. Several computer runs were made, with one or more force constants being adjusted manually each time, until a better fit was obtained. In the sixth run, sixteen force constants were refined by the least-squares part of MOLVIB to fit twenty-three wavenumbers. Several more runs were made with manual adjustments being made, and then in the final run, thirteen force constants were least-squares refined to fit twenty-three assigned wavenumbers. The average difference between calculated and observed values was a very low 1.9 cm^{-1}. The observed and calculated wavenumbers, along with a description of the vibrations in terms of localized symmetry coordinates, are listed in Table 1.[12]

The TNAZ/ADNAZ work showed a frequency shift of the (N)-NO_2 antisymmetric stretch band from 1537 cm^{-1} in neat TNAZ to 1553 cm^{-1} in a 50:50 (mol percent) mixture after melting and recrystallization.[1] In addition, the (N)-NO_2 out-of-plane wagging band shifted from 665 cm^{-1} to 650.[1] The proposed explanation was that either (1) internal rotation of the NO_2 groups results in a conformational change, as had been observed in DNNC,[10] or (2) component interaction produces minor changes in a few force constants. The IR spectra for a 35:65 (mol percent) TNAZ/NO-DNAZ mixture show the same behavior for TNAZ, with the shifts [from neat (and mixture prior to melting and recrystallization) to recrystallized mixture melt] of the two bands just mentioned being exactly the same as in the TNAZ/ADNAZ mixtures. It therefore seems that the conformational behavior of TNAZ is the same in a mixture with NO-DNAZ as it is in a mixture with ADNAZ. However, none of the bands due solely to NO-DNAZ show such a shift, so either this compound (1) does not undergo a conformational change, or (2) no bands above 500 cm^{-1} are dependent on conformation.

It was pointed out that both ADNAZ and TNAZ have several calculated wavenumbers to which observed values were not assigned.[1] This is also the case for NO-DNAZ, as shown in Table 1, where seven calculated values above 500 cm^{-1} do not have observed bands assigned to them. Of course, there are no observed values below 500 cm^{-1} because this was out of the range of the FTIR spectrometer. If only infrared spectra (and not Raman) are obtained for a compound with as

TABLE 1. OBSERVED AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTIONS FOR 1-NITROSO-3,3-DINITROAZETIDINE

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contributions to the P.E.D. in symmetry coordinates[b]
---	159	CN2 bend(59), NO2 out-of-plane wag(16)
---	173	CNN bend(71)
---	183	CN2 wag(39), CNN bend(24)
---	257	CN2 twist(62), NO2 out-of-plane wag(26)
---	285	NNO bend(18), CNN bend(15), CN2 wag(14), NO2 rock(12)
---	313	CN2 rock(52), NO2 out-of-plane wag(10)
---	369	CN stretch(28), ONO bend(16), CNN bend(12)
---	419	NO2 rock(43), CN stretch(15)
513	517	NO2 rock(23), NO2 out-of-plane wag(19), NNO bend(14)
---	535	NO2 out-of-plane wag(40), NO2 rock(14), CN2 twist(13)
594	590	NO2 out-of-plane wag(29), NNO bend(18)
663	664	CN2 wag(29), NO2 out-of-plane wag(27), NO2 rock(14)
708	699	ONO bend(27), CN2 rock(14), NO2 sym. stretch(12)
726	729	ONO bend(35), NO2 sym. stretch(12), NO2 out-of-plane wag(11)
812	810	NN stretch(20), NO2 sym. stretch(18), Ring deformation(13), CH2 wag(10)
855	853	Ring deformation(56)
913	914	CN stretch(36), CH2 rock(12)
---	1018	CH2 wag(37), NN stretch(34)
---	1060	Ring deformation(70), CN2 wag(11)

TABLE 1. (continued)

obs.[a] cm^{-1}	calc. cm^{-1}	Main % contributions to the P.E.D. in symmetry coordinates[b]
---	1088	CH2 twist(87), CH2 rock(11)
1101	1102	Ring deformation(32), CH2 wag(23), CNN bend(15)
---	1133	CH2 rock(79)
---	1150	CH2 twist(55), CH2 rock(25)
---	1165	Ring deformation(29), CH2 twist(12), NO2 sym. stretch(10)
1203	1203	CH2 wag(53), Ring deformation(26)
1263	1263	CH2 rock(34), NO2 sym. stretch(30)
1288	1288	Ring deformation(30), CH2 wag(21), CH2 bend(13), CH2 wag(10)
1333	1332	NO2 sym. stretch(28), CN stretch(28), ONO bend(14)
1333	1342	NO2 sym. stretch(35), CN stretch(26), ONO bend(17)
1383	1383	CH2 bend(78)
1421	1415	CH2 bend(42), CH2 wag(16), Ring deformation(15)
1421	1422	NO stretch(67), CNN bend(11)
1574	1574	NO2 asym. stretch(66), NO2 rock(17)
1574	1576	NO2 asym. stretch(86), NO2 rock(11)
2962	2962	CH2 sym. stretch(99)
2980	2980	CH2 sym. stretch(99)
3014	3014	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

many atoms as are in a molecule of NO-DNAZ, there are nearly always some vibrational modes that have intensities that are too low to be observed. This is due either to selection rules or to a very small change in the molecular dipole moment during the vibration. Infrared intensities were calculated for NO-DNAZ with the HyperChem™ program, and these calculations indicated that quite a few bands should be unobserved in the IR spectrum because of low intensity. This includes almost all the bands below 500 cm^{-1}. 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.

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, with the two NO_2 groups taking up different orientations in the two conformers.[10] However, no evidence of the presence of more than one stable conformation could be found in the case of NO-DNAZ. Molecular mechanics and semi-empirical molecular orbital calculations were made for NO-DNAZ in order to compare the results with the X-ray structure. A conformational search on the molecule was done with the HyperChem™ programs, with all three rotating groups being permitted to rotate during the search to find stable conformations. However, it is not likely that the nitroso group will rotate about the N-N bond because of the double-bond character to this bond, which will cause the barrier to internal rotation to be quite high.

The HyperChem™ MM+ molecular mechanics and the AM1 and PM3 molecular orbital programs were all used to do the conformational search. The results from all three programs were unsatisfactory, except as a good qualitative picture of what the structure is like. The AM1 ring is planar, and the N-N bond is only two or three degrees out of the CNC plane. The PM3 structure shows a slightly puckered ring (8° or 9°), but the N-N bond is about 35° out of the CNC plane. MM+ gives an even larger angle than this. The bond lengths are mostly unsatisfactory for all three programs. The nitroso N=O bond is calculated too short, as if it were a pure double bond, and the N-N and C-N bonds are all calculated too long by as much as 0.07 Å for C-N. The nitro N-O bond lengths are within 0.02 Å for AM1 and MM+ and within 0.01 Å for PM3. The C-C bonds are calculated to be 0.03-0.05 Å too long. AM1 and PM3 found only one stable conformation, but MM+ found a higher-energy form (by ca. 2.5 Kcal/mol) that had the nitroso oxygen rotated back over the ring.

CONCLUSIONS

Appropriate force constants from the modified valence force field that had been determined for TNAZ were transferred successfully to NO-DNAZ. Manual and least-squares adjustments of selected force constants resulted in an exceptionally low average error for the calculated wavenumbers that were assigned to observed values. The force field that was obtained should be useful in normal coordinate calculations of other substituted dinitroazetidines. Molecular mechanics and semi-empirical molecular orbital calculations with a commercial program did not give structures that agreed very well with the X-ray structure.

FINAL COMMENTS

The force constants, their definitions, and their final converged values are given in Table 2. Table 1 shows that the fundamental vibrational frequencies of NO-DNAZ can be reproduced satisfactorily with relatively minor changes in the values of the force constants that were transferred from TNAZ. However, in looking at the significance of the individual values of the force constants given in Table 2, the following points should be considered: (1) a slightly different set of force constants (i.e., using different interaction constants) can result in just as good a fit as the one that was used; (2) holding different sets of force constants fixed will result in different values of the refined constants, so there are many sets of force constants that will give a good fit of calculated to observed frequencies; (3) vibrational anharmonicity and crystal-field effects are neglected. For these reasons, the accuracy of the force constant values will be diminished. However, one of the purposes of doing normal coordinate calculations is to obtain force constants that are transferable to similar molecules. The property of transferability suggests some significance to the force field as a whole and therefore to the vibrational assignment from which the force field was obtained. Therefore, a given set of force constants is still useful in solving spectroscopic problems.

TABLE 2

Force constants for NO-DNAZ

Force Constant	Group	Atom(s) common	Value[a]
Stretch			
C-H	CH_2[b]	-	4.864
C-H	CH_2[c]	-	4.931
N-N	N-N-O	-	4.000
N-O	N-N-O	-	7.988
N-O	NO_2[d]	-	7.454
N-O	NO_2[e]	-	8.093
C-C	ring	-	4.450
C-N	ring	-	4.397
C-N	$C-NO_2$	-	4.100
Stretch-Stretch			
CH,CH	CH_2[b]	C	0.043
CH,CH	CH_2[c]	C	0.036
NO,NO	NO_2[d]	N	0.224
NO,NO	NO_2[e]	N	0.138
CC,CC	ring	C	0.100
CC,CN	ring	C	-0.060
CC,CN	CH_2CNO_2	C	0.600
CN,CN	ring	C	0.213
CN,CN	$C(NO_2)_2$	C	0.300
CN,NN	CH_2CNO	N	0.964
NN,NO	N-N-O	N	0.494

Table 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
CN,NO	CNO_2[d]	N	0.804
CN,NO	CNO_2[e]	N	0.800
Bend			
H-C-H	CH_2	-	0.350
N-C-H	N-CH_2	-	0.706
C-C-H	C-CH_2	-	0.702
N-N-O	N-N-O	-	1.435
C-N-O	C-NO_2[d]	-	1.200
C-N-O	C-NO_2[e]	-	1.393
C-N-N	C-N-N-O	-	1.200
C-C-N	C-CH_2-N	-	1.000
C-C-N	CH_2-C-NO_2	-	1.200
C-C-C	ring	-	1.200
C-N-C	CH_2-N-CH_2	-	1.330
N-C-N	$C(NO_2)_2$	-	1.600
O-N-O	NO_2	-	1.409
NO_2 o-p	CNO_2[d]	-	0.389
NO_2 o-p	CNO_2[e]	-	0.328
Stretch-Bend			
CC,CCH	C-CH_2	C-C	0.314
CC,CCN	CH_2-C-NO_2	C-C	0.712
CC,CCN	ring	C-C	0.200

Table 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
CC,CCC	ring	C-C	0.200
CN,CCN	ring	C-N	0.686
CN,CNN	CH_2-CNO	C-N	-0.029
CN,CNC	ring	C-N	0.110
CN,CCN	CH_2-C-NO_2	C-N	0.400
CN,CNO	C-NO_2[d]	C-N	0.300
CN,CNO	C-NO_2[e]	C-N	0.000
NN,CNN	CH_2-NNO	N-N	-0.029
NN,NNO	N-N-O	N-N	0.407
NO,NNO	N-N-O	N-O	0.085
NO,CNO	C-NO_2[d]	N-O	-0.182
NO,CNO	C-NO_2[e]	N-O	0.385
NO,ONO	NO_2[d]	N-O	0.100
NO,ONO	NO_2[e]	N-O	0.200
CN,ONO	C-NO_2	N	0.200
Bend-Bend			
NCN,CCN	C-C-$(NO_2)_2$	C	0.200
CNO,ONO	C-NO_2[d]	N	-0.154
CNO,ONO	C-NO_2[e]	N	0.110
CNO,CNO	C-NO_2[d]	C-N	0.000
CNO,CNO	C-NO_2[e]	C-N	0.100
CCH,CCH	C-CH_2	C-C	-0.078
CCH,NCH	C-CH_2-N	C-H	0.017

Table 2 (continued)

Force Constant	Group	Atom(s) common	Value[a]
NCH,NCH	$N(CH_2)_2$	N-C	-0.027
CNN,CNN	$N-N(CH_2)_2$	N-N	0.200

[a] Stretching constants are in units of mdyn/Å; stretch-bend constants are in units of mdyn/rad; bending constants are in units of mdyn Å/rad^2.

[b] front CH_2 group in Fig. 2

[c] back CH_2 group in Fig. 2

[d] top NO_2 group in Fig. 2

[e] bottom NO_2 group in Fig. 2

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11. A referee suggested that the N-N bond in a nitramine is a weak single bond and that the N-N bond length (1.292 Å) in the nitroso group is probably a better example of a typical N-N single bond.
12. Although the molecule has no symmetry, localized symmetry coordinates (e.g., for the NO_2 groups or the CH_2 groups, etc.) were used to aid in interpretation of the spectra. A CH_2 wagging symmetry coordinate, for example, would be constructed from the four internal coordinates C3-C2-H1, C3-C2-H2, N1-C2-H1, and N1-C2-H2 angles; it would be written as $S_{wag} = ½(\gamma_1 + \gamma_2 - \beta_1 - \beta_2)$, where the γ's and β's represent the angles just given.

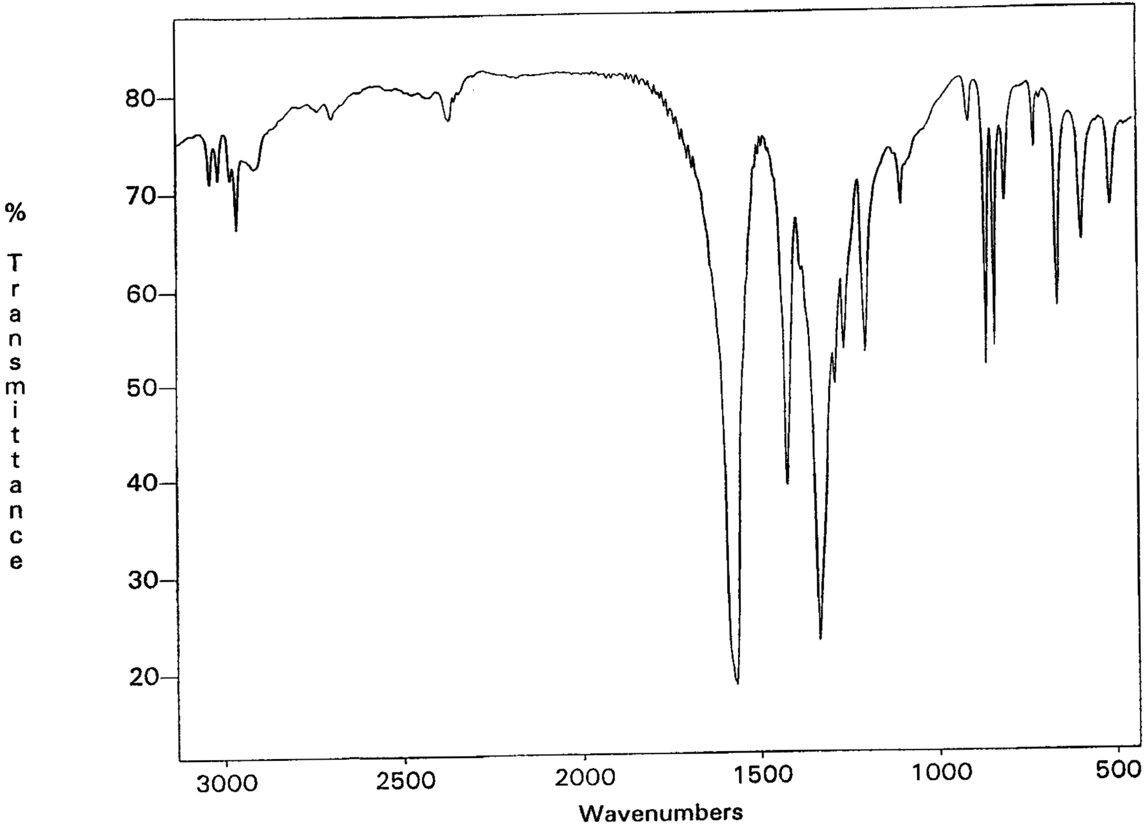

FIGURE 1

Infrared spectrum of NO-DNAZ (KBr Pellet)

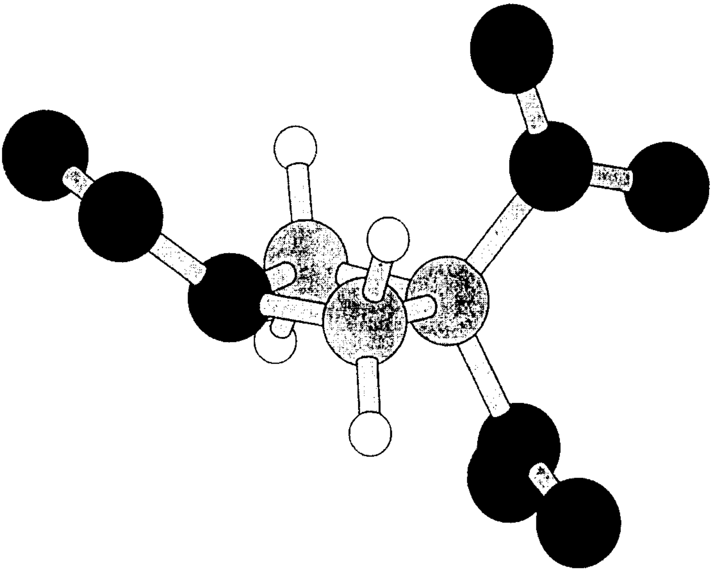

FIGURE 2

Ball-and-stick model of NO-DNAZ