The Infrared, Raman and NMR Spectra of Hexamethylene Triperoxide Diamine

D. Sülzle and P. Klaeboe

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

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The title compound 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane has been synthesized, and IR and Raman spectra of the solid compound recorded. Additionally, ^1H and ^{13}C NMR spectra of the compound in saturated DMSO-d_6 solution were obtained. A tentative assignment of the vibrational spectra was carried out in terms of D_3 molecular symmetry, established by an earlier X-ray crystallographic study. The NMR spectra indicate a similar molecular structure in DMSO solution.

The title compound 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane (hexamethylene triperoxide diamine; in the following abbreviated as HMTD) was first synthesized in 1885.[1] The compound was later shown to be an initiating explosive,[2] but since it decomposes slowly at room temperature it has not acquired importance as a military explosive. In two recent papers from police departments in Israel[3] and in USA,[4] the use of HMTD and the related triacetone triperoxide (TATP) was identified in several cases of terrorist activity. Both explosives are easy to prepare and the starting materials are readily available. Most important, however, is the fact that unlike common primary explosives such as lead azide or mercury fulminate, these peroxides (HMTD and TATP) contain no heavy metal atoms. Thus, they would easily pass the X-ray control of airport security procedures.

Because of the explosive properties of HMTD the general structure was assumed[5] to consist of two pyramidal $N(CH_2)_3$ groups connected by three peroxide linkages. Within this framework, different structures, including a cage-type molecule[5] or one consisting of two $\underline{\mathrm{COOCN}}\mathrm{{-}C}$ moieties connected by an O−O bridge, have been proposed. The exact geometry was recently established by single-crystal X-ray diffraction.[6] HMTD was found to have a cage structure and to possess D_3 molecular symmetry. Moreover, it crystallizes in the trigonal space group *R3m* with three molecules in the unit cell. Surprisingly, the two nitrogen atoms have planar 3-fold coordination[6] with CNC angles all equal to 120°. The carbon analogue of HMTD (1,6-diazabicyclo[4.4.4]tetradecane) also has D_3 symmetry, but the two NCCC groups of this molecule are both pyramidal with *in* configuration[7] (i.e. the nitrogen lone-pair points towards the cavity of this compound). Surprisingly, inside protonation of the carbon analogue results in a contraction of the N,N′ non-bonded distance (from 2.806 to 2.526 Å),[7] whereas in HMTD with an N,N′ distance of 3.193 Å inside protonation was not achieved.[6]

Because of the interesting molecular structure of HMTD (shown in Fig. 1) we decided to carry out an infrared and Raman spectroscopic study of this molecule. Previously, no Raman spectra and only routine IR spectra in restricted regions[4,5] have been published, with limited attempts at spectral interpretations.[5]

Experimental

Preparation. HMTD was prepared according to an established procedure from hexamethylene tetramine, 30 % hydrogen peroxide and citric acid.[6] The product was obtained in ca. 40 % yield and was recrystallized from a large excess of ethanol

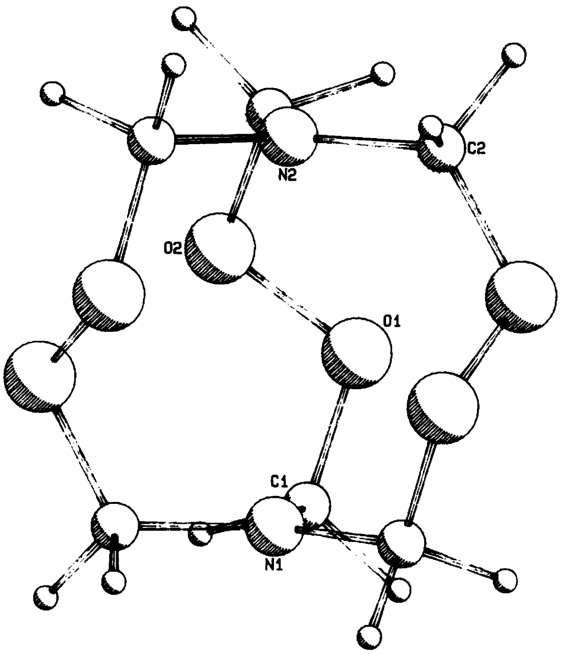

Fig. 1. The molecular geometry of HMTD oriented with the three-fold axis vertical.

(1 l per g HMTD). A melting point of 144–5 °C for the white crystals was established. However, since HMTD is highly explosive *it should not be heated to melting without taking great precautions.* In some cases it exploded before melting. At the melting point it decomposed rapidly and turned yellow.

Instrumental. The IR spectra were recorded on a Perkin-Elmer model 225 grating spectrometer (4000–200 cm^{-1}), on a Perkin-Elmer model 1700 FTIR spectrometer (4000–500 cm^{-1}) and on an evacuated Bruker FTIR model 114 c (700–50 cm^{-1}) spectrometer. HMTD is practically insoluble in non-polar solvents (CS_2, CCl_4, C_6H_6, C_6H_{12}) and only very slightly soluble in dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMFA). No IR spectra of HMTD in solution could therefore be recorded. No attempts were made to record melt spectra because of the rapid decomposition of the compound at the melting temperature (see above). Moreover, we were re-

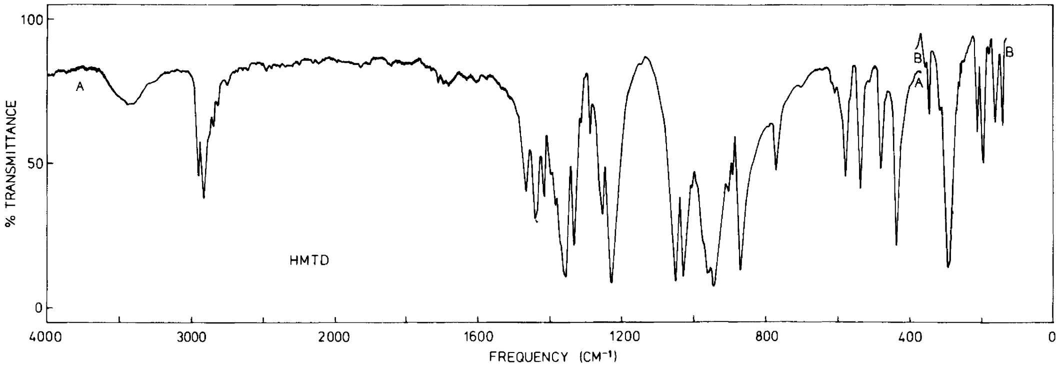

Fig. 2. IR spectra of hexamethylene triperoxide diamine (HMTD) in (A) KBr and (B) polyethylene pellets.

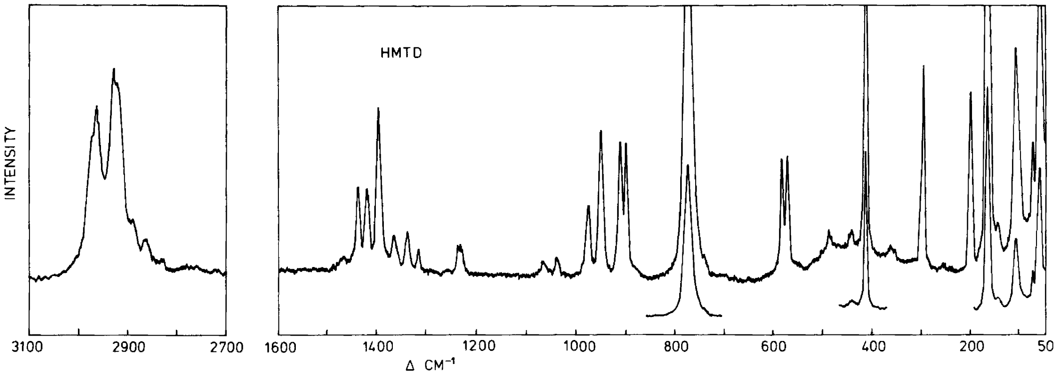

Fig. 3. Raman spectrum of HMTD as a polycrystalline solid.

luctant to heat an explosive like HMTD above room temperature on the basis of our experience with several highly explosive unsaturated azides recently investigated in this laboratory.[8] For these reasons, HMTD was studied as pellets in KBr and polyethylene, and as a Nujol mull between CsI plates.

Raman spectra were obtained with a Dilor model RT30 spectrometer (triple monochromator) interfaced to the Aspect 2000 computer of the Bruker spectrometer. An argon ion laser (Spectra Physics model 2000) was employed for excitation, using the 514.5 nm line and an interference filter to remove unwanted plasma lines from the laser emission. The polycrystalline sample of HMTD was illuminated in the 90° and 180° geometries with approximately 75 mW of laser power. In one case the output was increased to ca. 150 mW, whereupon the sample exploded violently in front of the lens.

Proton and ^{13}C NMR spectra of saturated solutions of HMTD in DMSO-d_6 were recorded on a Bruker model CXP-200 (^1H), and on a Varian model XL-300 spectrometer at 300 MHz (^1H) and at 75 MHz (^{13}C).

Results

The IR spectra of HMTD in KBr and polyethylene pellets are shown in Fig. 2, and a Raman spectrum of the solid is shown in Fig. 3. Both spectra were obtained with a freshly prepared sample, recrystallized from ethanol. It was observed that the compound slowly decomposes on storage, as was apparent from the appearance of an IR band at 1680 cm^{-1}. This band, also present in previously published spectra,[4] must be attributed to a carbonyl moiety. Possibly, aldehyde groups are formed by cleavage of one of the O–O bonds. Even when the 1680 cm^{-1} impurity band became reasonably strong, no significant changes in other regions of the spectrum were detected.

The ^1H NMR spectrum recorded at 295 K in DMSO-d_6 is presented in Fig. 4. Corresponding spectra were recorded at higher temperatures. At 298 K the proton peaks were situated at 4.644, 4.689, 4.777 and 4.823 ppm, while at 323 K they were found at 4.624, 4.691, 4.768 and 4.835 ppm. The "outer" lines appeared as small shoulders at 373 K, whereas the "inner" lines were found at 4.701 and 4.752 ppm.

All these ^1H spectra had a quartet around 2.5 ppm (2.498, 2.505, 2.511 and 2.516 ppm) and a broad line at 3.336 ppm which are due to impurities of DMSO-d_5 and water, respectively, in the hydroscopic solvent. The high intensities of these DMSO impurity lines, compared with the four HMTD proton peaks around 4.7 ppm, illustrate the low solubility of HMTD even in this most favourable solvent. The proton-decoupled ^{13}C NMR spectrum consisted of a single line for HMTD (δ = 89.9 ppm) in addition to the DMSO-d_6 lines around 40.0 ppm.

Interpretation

The infrared and Raman spectra have been interpreted in terms of the D_3 symmetry established for the solid compound by X-ray diffrac-

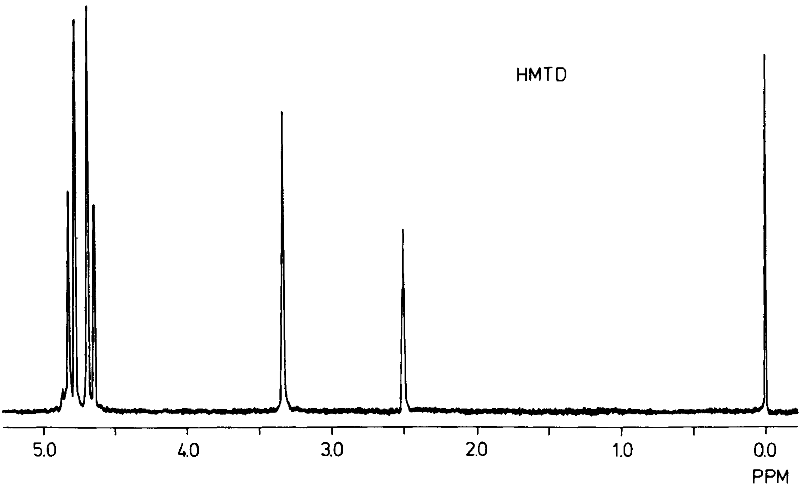

Fig. 4. The ^1H NMR spectrum of HMTD in a saturated solution in DMSO-d_6 at 298 K.

tion.[6] With 26 atoms, the molecule has 72 vibrational degrees of freedom. The vibrations will divide themselves into 13 A_1 (Raman active), 11 A_2 (IR active) and 24 doubly degenerate E modes (IR and Raman active).

Raman polarization spectra of HMTD in solution would be desirable, and would make possible a distinction between the Raman active A modes (polarized) and the E modes (depolarized). While the solubility in non-polar solvents was much too low, the highly polar solvents DMSO and DMF were tried. Certain intense HMTD bands could just barely be detected in solution, but the spectra were of very poor quality due to low solubility and intense solvent bands. Thus, no reliable polarization data were obtained in solution, and melt spectra were ruled out owing to the instability of HMTD (see above). Moreover, no single crystal of a size suitable for a Raman investigation could be grown, and neither could an oriented polycrystalline sample suitable for IR dichroism measurements be prepared. With these limitations, the spectral assignments into A_1, A_2 and E species have to rely upon the coincidence or non-coincidence of IR and Raman bands.

Table 1. A representation of the vibrational modes of hexamethylene triperoxide diamine (HMTD) in terms of localized motions.

Localized Motions	Expected region	Species		
		A_1	A_2	E
CH_2 str out of phase	2950	1	1	2
CH_2 str in phase	2850	1	1	2
CH_2 scissor	1450	1	1	2
CH_2 wag	1400	1	1	2
CH_2 twist	1300	1	1	2
N–C str	1100	1	1	2
C–O str	1000	1	1	2
O–O str	900	1		1
CH_2 rock	700	1	1	2
COO def	500	1	1	2
NCO def	400	1	1	2
CCCN out of plane bend	<300	1	1	
CCCN in plane bend	<300			2
O–O torsion	<300	1		1
Number of modes		13	11	24

The valence stretching or bending coordinates of HMTD can be made a basis for a representation of the group D_3. By this procedure a distribution of the normal vibrations into the different symmetry species can be made according to the localized stretching or bending coordinates, as shown in Table 1. To a first approximation we therefore expect the A_1, A_2 and E vibrations associated with the same valence coordinate to appear in the same wavenumber region. Some of the vibrations, such as the CH_2 out-of-phase and in-phase stretch, CH_2 scissor and CH_2 wag, are highly localized and appear in well-defined re-

Table 2. Observed IR and Raman wavenumbers and tentative assignments of the HMTD spectra.

IR[a] pellet	Raman solid	Species
	2977 m, sh[b]	Comb
2961 vs	2966 s	ν_{14} A_2
		ν_{25} E
	2929 vs	ν_1 A_1
2924 vs	2921 m	ν_{26} E
2880 m, sh	2891 w	ν_{27} E
	2866 w	ν_2 A_1
2859 m		ν_{15} A_2
2827 m	2830 w	ν_{28} E
2966 w		Comb
1465 s	1470 w	ν_{29} E
1456 s		ν_{16} A_2
1447 s	1449 vw	ν_{30} E
1436 vw	1440 s	ν_3 A_1
1422 w	1420 s	ν_{31} E
1419 w		Comb
1403 vw	1405 vw	Comb
	1398 vs	ν_4 A_1
1387 vw	1389 vw	ν_{32} E
1376 m		ν_{17} A_2
1361 vs, br	1365 m	ν_{33} E
	1342 m	ν_5 A_1
1337 s		ν_{18} A_2
1318 vw	1320 w	Comb
1293 vw	1295 vvw	Comb
1257 m	1261 vw, br	ν_{34} E
1233 vs	1237 m, br	ν_{35} E
	1068 w, br	ν_6 A_1
1054 s		ν_{19} A_2
1045 vvw	1040 m	ν_{36} E
1033 s		ν_{20} A_2
1024 vw		Comb
1010 vw		Comb
978 m, br	975 m	ν_{37} E
966 s		ν_{21} A_2
950 s	950 s	ν_{38} E
	930 vw	ν_7 A_1
908 vw	910 s	ν_8 A_1
898 w	899 s	ν_{39} E
877 vw		Comb
875 s	876 vvw	ν_{40} E
863 w, sh		Comb
798 vvw		Comb
777 w		Comb
	773 vs	ν_9 A_1
701 vw		Comb
621 vw		Comb
612 vvw		Comb
594 vvw		Comb
584 w	584 m	ν_{41} E
573 vvw	573 m	ν_{10} A_1
543 m	547 vw, sh	ν_{42} E
516 w		ν_{22} A_2
486 m	487 w	ν_{43} E
441 m	444 w	ν_{44} E
	413 vs	ν_{11} A_1
396 vw		Comb
362 vw	364 vw, br	Comb
	355 vw	Comb
348 w		ν_{23} A_2
324 vw	325 vw	Comb
299 m	301 m, sh	ν_{45} E
	297 s	ν_{12} A_1
222 w		ν_{24} A_2
202 w	201 s	ν_{46} E
	198 w, sh	Comb
	169 vs	ν_{13} A_1
142 vw	146 w	ν_{47} E
108 w	109 s	ν_{48} E
	101 w, sh	Lattice
78 w		Lattice
	63 vs	Lattice
	46 w	Lattice

[a] KBr pellet above 500 cm^{-1}, PET pellet below 500 cm^{-1}. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

gions. In particular, in the bicyclic cage-like structure of HMTD (Fig. 1) the skeletal stretching and bending modes will be highly mixed and will appear in spectral regions which are difficult to predict. Therefore, the expected regions given for the localized motions in Table 1 should be considered as guide lines, and not be applied literally to all the assignments of Table 2. Owing to the unusual structure of HMTD, with planar NCCC moieties, both stretching and bending force constants were difficult to predict. For this reason we did not carry out a force constant calculation for this molecule.

The results of the spectral interpretations have been included in Table 2 together with the complete list of IR and Raman bands observed. The following general procedure was followed: (1) All the very strong, strong or medium intensity bands observed in IR or in Raman spectra with no counterpart in the other spectrum are assigned as A_2 and A_1 fundamentals, respectively. (2) Coinciding IR and Raman bands (within 4 cm^{-1}) in which at least one of the components has very strong, strong or medium intensity bands are regarded as E modes. (3) Weak or very weak IR and Raman bands observed alone or present in both spectra are regarded as combination bands or overtones.

To make reasonable assignments, we had to make some exceptions to these rules; thus, the weak IR bands at 516, 348 and 222 cm^{-1} with no Raman counterparts were interpreted as the A_2 modes ν_{22}, ν_{23} and ν_{24}. Similarly, three Raman bands at 2866 w, 1068 w and 930 vw are assigned as the A_1 modes ν_2, ν_6 and ν_7, respectively. The IR and Raman pairs around 1388 and 144 cm^{-1} are interpreted as the E fundamentals ν_{32} and ν_{47} although both the IR and Raman components are weak or very weak. Finally, the IR and Raman pairs at 908 vw (IR), 910 s (R), and 573 vvw (IR) and 573 m (R) are assigned as A_1 rather than E fundamentals.

Although the spectral assignments of Table 2 should be considered as tentative, the results are in good agreement with the D_3 molecular symmetry. With the large number of fundamentals of HMTD we did not attempt to explain the various combination bands, since alternative explanations could be proposed in most cases.

The NMR results strongly support the assumption that HMTD retains D_3 symmetry in solution. Thus, the single peak (δ = 89.9 ppm) in the ^{13}C NMR spectrum reveals that all 6 carbon atoms are symmetrically equivalent. The proton spectrum (Fig. 4) contains four proton peaks in addition to the water and DMSO-d_5 lines (see above). From Fig. 4 it can be seen that the four lines around 4.7 ppm apparently form an AB spectrum with chemical shift $\delta_A - \delta_B = 0.126$ ppm and coupling constant $J_{A,B} = 0.046$ ppm. Moreover, from the observed line positions the intensity ratio between the two "inner" lines and the two "outer" lines was predicted to be 2.03. The experimental intensity ratio was 1.87 at 298 K, in reasonable agreement with the prediction. At 323 K the predicted intensity ratio was 2.74, to be compared with the experimental value of 2.83.

The ^1H NMR spectrum of HMTD is consistent with two sets of equivalent hydrogens of the same abundance as expected from the D_3 symmetry of HMTD. A lower (e.g. C_3) or higher (e.g. D_{3h}) symmetry in solution would not be in accordance with the observed AB spectrum.

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