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Rapid Communication

The ^{14}N quadrupole coupling in hexamethylene triperoxide diamine (HMTD)

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Abstract

Using high-field NMR, we have determined the magnitude of the nuclear quadrupole interaction in hexamethylene triperoxide diamine (HMTD), the explosive allegedly used in the London bombings of July 2005. The experimental quadrupolar coupling constant, 5.334 MHz, is in good agreement with quantum chemical calculations. The predicted single zero-field transition frequency should lie in a relatively empty part of the ^{14}N nuclear quadrupole resonance (NQR) spectrum; the spin relaxation rate is reasonably fast.

Keywords: NMR, ^{14}N, peroxide, HMTD, electric field gradient, *ab initio*
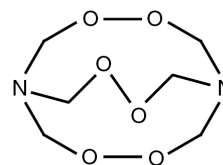
Introduction

Hexamethylene triperoxide diamine (HMTD), probably discovered at the end of the 19th century,[1] languished in relative obscurity for 100 years, until its ease of preparation and stability relative to other organic peroxides, attracted the interest of terrorists, most notably the perpetrators of the London bombings of 2005.

HMTD is an interesting molecule to the physical chemist; it is helically chiral in solution[2] but crystallizes with disorder[3] in the achiral space group $R3m$[4]; the nitrogens lie on the crystallographic threefold axis. It possesses a comparatively planarized tertiary nitrogen, largely a result of the electron-withdrawing character of the peroxide groups ringing its molecular equator.[5] Because of the local symmetry, the chemical shielding and electric field gradient (EFG) tensors are constrained to be axially symmetric, with the unique axis perpendicular to the pseudo-plane. Pure quadrupole resonance is an established method for the detection of explosives and other contraband, and characterizing the ^{14}N HMTD NMR properties of HMTD is therefore a matter of more than academic interest. However, the desirability of working with small amounts of this unstable material, combined with the inherent low sensitivity of pure quadrupole resonance, led us to approach the initial characterization of the ^{14}N resonance of this material by high-field NMR.

Experimental

HMTD was prepared by standard methods;[4] NMR experiments were conducted at 14 T in a Bruker Avance spectrometer equipped with high-power amplifiers for solids. The probe was homebuilt, with a 1.1cm × 1 cm (diameter × length) coil, tunable over the range 35–90 MHz. The [14]Nπ/2 pulse, measured for [14]NH$_4$Cl at the Zeeman frequency, was 8 μs; because the NMR signal of HMTD was expected greatly to exceed the bandwidth of the instrument, and thus only single transitions excited, an effective single transition π/2 pulse of 5.7 μs ~ (8 μs/√2) was used in all experiments. Although there are no reports that high radio frequency fields can induce detonation of this material, to guard against this possibility, the NMR probe, with the screws on the top removed to allow it to blow out, was placed behind an explosion-proof screen, and the sample subjected to 30 μs pulses, once per second for 10 min, at a power level 2 dB above operating levels, before it was inserted into the NMR magnet. To detect signals of HMTD, a Hahn echo sequence (π/2 – τ – π – τ – acquire) was employed, with τ delays of 80 μs and delays between acquisitions of 8 s; typically 1000 transients were averaged to obtain a spin echo. Echoes were obtained every 200 kHz over two regions, each spanning 1 MHz, at 1.9 MHz above and below the Zeeman frequency, where computations suggested the perpendicular edges of the Pake doublet were likely to lie. Once the

peak intensities of the Pake doublet were located, higher quality spin-echo spectra were obtained centered at or near the estimated frequency.

The relaxation behavior of HMTD was characterized by progressive saturation; echo intensities were accumulated at the frequency of the upper parallel edge using the standard spin-echo sequence, and recycle delays between 1 and 32 s.

Results

Figure 1 shows the results of the echo sweep. Two pronounced maxima are apparent; the lower maximum, at 41.36 MHz is less intense than the upper maximum at 45.36 MHz, partly because of the relative Boltzmann polarizations and detection efficiencies of the two transitions, but more importantly because of the better coincidence of the upper transition maximum with the Pake-doublet perpendicular edge (see below). Such frequency sweep measurements are necessarily coarse-grained and limited in accuracy. The spectra shown in Figure 2(a) are Fourier transforms of spin-echo free-induction decays (FIDs) acquired at frequencies of 41.406241 and 45.406241 MHz, respectively. These spectra allow careful examination of the Pake-doublet perpendicular edge, and they were fit to simulated Pake doublets, computed to second order in perturbation theory, assuming an axially symmetric quadrupolar coupling tensor, using a finite pulse width correction for the spin-echo response using the measured 5.7 μs π/2 pulse length; fit parameters were C_Q = 5.3346 ± 0.001 MHz, T_2^* =177 μs, and $\sigma_\perp$ (offset of the HMTD perpendicular edge relative to NH_4Cl, presumably as a result of chemical shielding tensor of HMTD) = + 0.002 ± 0.001 MHz. In fact, the relative sparseness of the Hamiltonian allows us to derive an exact formula for the perpendicular edges.

$$\nu_\perp = \sqrt{\nu_0^2 + \frac{9}{64}C_Q^2} \pm \frac{3}{8}C_Q \qquad (1)$$

where ν_0 is the nuclear Larmor frequency. At this orientation, there are no odd-order terms in C_Q except for the first-order; the fourth-order shift, the largest term omitted from the simulation, is predicted to be 24 Hz at the perpendicular edge.

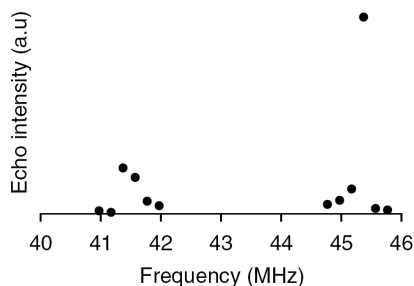Segments of the simulations corresponding to the same frequency ranges as the experimental spectra are shown in Figure

Figure 1. Intensity of the ^{14}N Hahn spin echo signal obtained from HMTD, as a function of spectrometer resonance frequency.
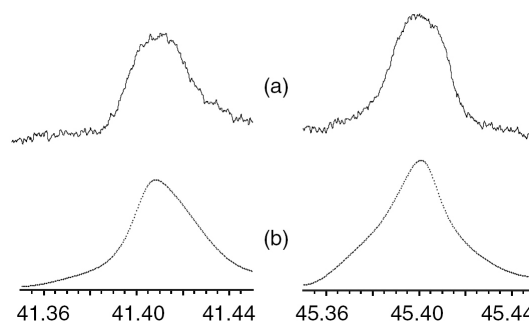

Figure 2. NMR spectrum of the two perpendicular edges of the HMTD ^{14}N Pake doublet, obtained by Fourier-transformation of the spin echoes, compared with simulated spectra, computed as described in the text.

2(b). The simulations are quite satisfactory, but the experimental spectra appear to contain an approximately 10 KHz additional frequency dispersion, manifest as a rather flat-topped lineshape which is not accounted for in the simulation; the most probable explanation for this is a dispersion in quadrupole constants due to the known crystallographic disorder.

Using a ^{14}N quadrupole moment eQ of 2.05 ± 0.02 fm[25] and the conversion factor K_Q = 2,349,647.8 Hartree^{-1} Bohr^2 fm^{-2}s^{-16};the *zz* element of the EFG tensor in atomic units (Hartree Bohr^2) is given by V_{zz} = C_Q/(eQK_Q) = 1.107 ± 0.01 au

HMTD calculations (Table 1) used the optimized D_3 structure published previously.[2] In order to examine the effects of larger basis sets and/or higher levels of correlation, we also examined EFGs for the open-chain analog of HMTD, tris(m ethylperoxymethylene)amine (TMPMA), using an optimized structure published previously[2]; trimethylamine (TMA) optimized at the B3LYP/6–311+ +G(2d,p) level; TMA optimized at the same level with the nitrogen constrained to 20 pm above the plane containing the carbon atoms (thus giving a more planar nitrogen with similar geometry to TMPMA, and denoted by the abbreviation TMA20); and ammonia. Calculations used the augmented, correlation-consistent polarized valence multiple zeta (aug-cc-pV*n*Z) basis set series of Dunning[7]; unlike the Pople basis sets, these allow a systematic comparison of EFGs calculated at different levels of theory, converging to the complete basis set (CBS) result, which was obtained using the formula of Woon and Dunning.[8]

$$V_{zz}(n) = V_{zz}(\infty) + B \exp(-nC) \qquad (2)$$

This formula was chosen for reasons of simplicity, and because there is no empirical or theoretical reason to chose more recent improvements. In any case, the exact formula used for the extrapolation makes relatively little difference to the result.

Electron correlation was introduced using second-order Møller–Plesset perturbation theory (MP2), as well as (where possible) coupled cluster-singles/doubles methods (CCSD). The latter accounts for the effect of correlation on EFGs very accurately. DFT calculations using the B3LYP functional are provided for the purposes of comparison. Unfortunately, coupled cluster calculations were not feasible for HMTD itself,

Table 1. Computed values of V_{zz}, in atomic units, obtained as described in the text

HMTD	RHF	B3LYP	MP2	
aug-cc-pVDZ	1.294588	1.159302	1.027761	
aug-cc-pVTZ	1.314485	1.208295	1.087333	
aug-cc-pVQZ	1.338141	1.234013		

TMPMA	RHF		B3LYP	
aug-cc-pVDZ	1.290172		1.151623	
aug-cc-pVTZ	1.313026		1.201484	

TMA	RHF	B3LYP	MP2	CCSD
aug-cc-pVDZ	1.234173	1.148088	1.055395	1.103184
aug-cc-pVTZ	1.275131	1.217830	1.131875	
aug-cc-pVQZ	1.297480	1.243632		
aug-cc-pV5Z	1.299655	1.255766		
CBS	1.306267	1.262187		

TMA-20	RHF	B3LYP	MP2	CCSD
aug-cc-pVDZ	1.464650	1.383545	1.279249	1.326223
aug-cc-pVTZ	1.498449	1.450323	1.357437	
aug-cc-pVQZ	1.524153	1.480579		
aug-cc-pV5Z	1.526928	1.495514		
CBS	1.538490	1.507743		

NH3	RHF	B3LYP	MP2	CCSD
aug-cc-pVDZ	0.900208	0.828925	0.751733	0.795296
aug-cc-pVTZ	0.922641	0.870354	0.800613	0.843492
aug-cc-pVQZ	0.946155	0.896108	0.823014	
aug-cc-pV5Z	0.947340	0.904913	0.824235	
CBS	0.960873	0.918792	0.829434	

but were run at the valence double-zeta (aug-cc-pVDZ) level for TMA and TMA20, and at the aug-cc-pVDZ and valence triple-zeta (aug-cc-pVTZ) levels for ammonia.

Increasing the basis set size systematically increased the EFG at nitrogen for all molecules at all levels of correlation. Unfortunately, the three Hartree–Fock calculations of HMTD are insufficient to do a CBS extrapolation. However, we were able to obtain CBS extrapolations for the Hartree–Fock results for TMA, TMA-20 and NH$_3$. The CBS result exceeds the aug-cc-pVTZ value by 0.0311, 0.0400, and 0.0382 respectively. It seems, therefore, reasonable to conclude that the CBS result for HMTD exceeds the aug-cc-pVTZ result by 0.0365 ± 0.0047.

While this is not the case for smaller basis sets, results for TMA, TMA20, and ammonia indicated that basis sets at the aug-cc-pVTZ level and higher, corrections for basis set incompleteness and electron correlation were largely additive. The difference between CCSD and MP2 EFGs fall in the range 0.0428–0.0469, with the lowest values being for ammonia.

The (CCSD–MP2) EFG appeared to be almost independent of basis set size, as one would expect if the corrections were additive. Therefore, we used an average of the four computations
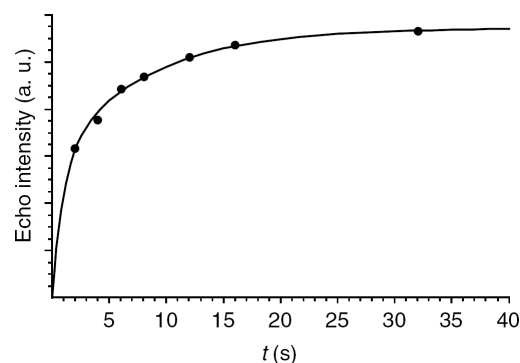

Figure 3. (Points) Intensity of the HMTD ^{14}N spin echo, obtained at the upper Pake-doublet perpendicular edge, as a function of the relaxation delay; (line) best least-squares fit to a biexponential recovery, composed of two equal components with fit-time constants of 1.0 and 8.0 s.

for which both CCSD and MP2 calculations were available, to estimate $V_{zz}(\text{CCSD}) - V_{zz}(\text{MP2}) = 0.0453 \pm 0.0025$.

Using these two corrections, we can now estimate a CCSD/CBS value for HMTD of 1.170 ± 0.006. For comparison, the same corrections applied to the MP2/aug-cc-pVTZ V_{zz} of TMA lead to an estimated CCSD/CBS value of 1.215 ± 0.006, compared with the experimental gas phase value of 1.159 ± 0.016 (computed from the microwave spectroscopic value of CQ D 5.5002 ± 0.0018 MHz).[9]

^{14}N spin relaxation under circumstances of single-transition excitation, as in the present case, is expected to be biexponential.[10] We can write the polarization of the 0–1 transition as the difference in population of the two respective spin states:

$$I_{01} = p_0 - p_1 \tag{3}$$

We can also write similar expressions for the Zeeman and quadrupolar polarization of the system

$$I_Z = p_{-1} - p_1 \tag{4}$$

$$I_Q = 2p_0 - p_1 - p_{-1} \tag{5}$$

Solving these three equations gives

$$I_{01} = \frac{(I_Z + I_Q)}{2} \tag{6}$$

or in other words, the single-transition polarization is an equal admixture of Zeeman and quadrupolar polarization. The experimental progressive-saturation echo intensity (Figure 3) gives an excellent fit to a biexponential decay with equal components; the two relaxation time constants are $T_{1Z} = 1.0$ s and $T_{1Q} = 8.0$ s; the shorter time constant is assumed to correspond to Zeeman order, since Zeeman and not quadrupolar order will be relaxed by fluctuations of the dominant quadrupolar interaction.

DISCUSSION

Observation of an axially symmetric Pake doublet from the ^{14}N signal of HMTD confirms the threefold symmetry of the

molecule required by the crystal structure, and the comparative narrowness of the perpendicular edge indicates that the crystallographic disorder has only a weak influence on the field gradient. Also, the very small inhomogeneous line width in this system has interesting consequences for the scheme used to detect the resonance signal. In the absence of line-broadening, theory requires that the intensity of the perpendicular edge of a Pake doublet diverges. While, in practice, no sample has zero intrinsic line width, in the present example the line width is about a factor of 3,000 smaller than the total width of the pattern, and the result is that the spin-echo intensity at the perpendicular edge is almost 20 times the intensity in the center of the pattern. This has important consequences for the measurement of ^{14}N quadrupole couplings, because it shows that the edges, from which the principal values can most accurately be determined, can be measured with much better sensitivity than the bulk of the pattern. Our data also indicate that the ^{14}N nuclear quadrupole resonance (NQR) spectrum will be correspondingly narrow, which should favor detection of this species at zero field.

The short Zeeman T_1 and longer quadrupolar T_1, suggests that relaxation is dominated by fluctuations in the large quadrupole coupling constant. Given the axial symmetry of the system, only the quadrupolar T_1 will be directly observable at zero field. The T_{1Q} value is quite long, presumably reflecting very limited dynamics in the crystal; however, it is probably not long enough to seriously inhibit zero-field observation of this material.

The similarity of the EFG to that of TMA was somewhat surprising, since the nitrogen in HMTD is nearly planar, and planarization of TMA leads to a considerable increase in the EFG, as a result of the increase in the *p*-character of the nonbonding orbital. In earlier work[2] we obtained an optimized structure of the open-chain analog of HMTD, TMPMA. Hartree–Fock EFGs for the optimized TMPMA structure were 1.2902 and 1.3130 at the aug-cc-pVDZ and aug-cc-pVTZ levels respectively, within 0.5% of those of HMTD at the same level of theory and much smaller than those at TMA-20, although the latter has the same degree of a planarity at the nitrogen. We therefore conclude that the increased *p*-character of the nonbonding electrons in HMTD, caused by planarization, is offset by electron withdrawal by the electronegative, peroxy groups. The comparable EFGs of HMTD and TMA, therefore, appear to be a result of the two competing and nearly equal, but oppositely signed, effects.

Assuming that we make the usual assumption that CCSD accurately accounts for electron correlation, the computed C_Q values of both HMTD and TMA exceed the experimental values by 5–7%. There are probably two contributions to the deviation; vibrational averaging, particularly by the umbrella mode along the molecular C_3 axis, and the failure of standard basis sets to adequately allow Sternheimer polarization of the nitrogen K-shell.[11,12] Comparing these results with those obtained with less accurate methods of correlation, it appears that in every instance, MP2 overestimates the correlation contribution to the EFG, by 33% to as much as 55%, while B3LYP underestimates the contribution by an even larger factor. Neither method, therefore, seems to constitute a satisfactorily quantitative way of dealing with correlation at tertiary nitrogens of this sort, and use of CCSD or other higher-level EC methods seems to be mandatory for such systems.

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