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Molecular structure and vibrational analysis of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene-α-d_3

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Abstract The X-ray structures of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene-α-d_3 have been determined at 130 K. The molecular structure and vibrational spectra are calculated by the MNDO-PM3 method, and are in agreement with experimental results. The short intra- and intermolecular hydrogen contacts correlate with the known thermal and ionization degradation pathways of 2,4,6-trinitrotoluene.

INTRODUCTION

In earlier studies [1–3], the vibrational spectra of 2,4,6-trinitrotoluene (TNT) in solid, liquid, and vapor phases have been compared with vibration frequencies calculated by using semi-empirical quantum mechanical models. The structures predicted theoretically were in reasonable agreement with that found in a room temperature X-ray diffraction study [4] for the average of the two independent molecules (designated forms A and B both here and in Ref. [4]) in the unit cell. The experimental structures, however, showed unreasonably large variations in both the C–C (1.364–1.408 Å) and C–N (1.443–1.496 Å) bond distances, which prompted the low temperature (130 K) redetermination of the crystal structure which we now report. We have also determined the structure of TNT-α-d_3 at 130 K to obtain additional verification on the short inter- and intramolecular hydrogen contacts (potential hydrogen bonds) that were reported in the previous study [4]. Finally, we have recalculated both the predicted molecular structure and the predicted gas-phase vibration spectrum using the MNDO-PM3 [5, 6] method.

EXPERIMENTAL

The synthesis of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene-α-d_3 have been described elsewhere [7]. Crystals of each compound suitable for X-ray analysis were cut from larger ones grown by the slow evaporation of solutions of the compounds in *n*-propanol (TNT) or *n*-propanol-OD (TNT-d_3). Data were collected at 130 K on a low temperature-accessorized Syntex P2$_1$ diffractometer.

THEORETICAL

The calculations were accomplished with the MOPAC program [8] using the MNDO-PM3 method [5, 6]. The MNDO-PM3 method uses optimized parameters that represent a considerable improvement over those parameters used with AM1 [9] and other semi-empirical methods. Typically, use of these parameters results in a significant decrease in heats of formation errors [6]. All ground state geometries were optimized using the BFGS function minimization procedure [10–13]. The Hessian matrix for the normal coordinate analysis was calculated as described previously [1].

RESULTS AND DISCUSSION

The heavy atom bond distances and bond angles obtained from the low temperature X-ray structures of 2,4,6-trinitrotoluene and 2,4,6-trinitrotoluene-α-d_3, and the corresponding dimensions of TNT calculated by the MNDO-PM3 method are given in Tables 1 and 2. The estimated standard deviations of the heavy-atom dimensions are: angles 0.4 (TNT) or 0.4–0.5 (TNT-d_3); C–C bonds 0.006–0.007 Å (TNT) or 0.007 Å (TNT-d_3); C–N and N–O bonds 0.005–0.006 Å (TNT) or 0.006–0.007 Å (TNT-d_3).

In general, the bond distances found in the present low temperature studies are in better agreement with those calculated by the MNDO-PM3 method than are the corresponding distances obtained in the previous room temperature structure determination [4]. The ring C–C bond distances span a much narrower range in the low temperature structures and the C–N bond distances are also closely similar.

The dihedral angles between the ring planes and the nitro groups differ by only a few degrees from those found in the earlier study, as shown in Table 3. The oxygen atoms on the *o*-nitro groups that are nearest the methyl group lie on the same side of the ring plane. In the calculated structure (gas phase) the 4-nitro group is almost coplanar with the phenyl ring, stabilized by hydrogen interactions as shown in Fig. 1, while those in the 2- and 6-positions are significantly twisted out of this plane.

The present study confirms the existence of the various short intra- and intermolecular hydrogen contacts (hydrogen bonds?) identified in the earlier

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Table 1. Bond distances (Å) and bond angles (degrees) for form A TNT and TNT-d_3

	TNT		TNT-d_3		TNT		TNT-d_3
Distance*	Obs.	Calc.	Obs.	Angle	Obs.	Calc.	Obs.
C1–C2	1.509	1.487	1.495	C1-C2-C3	123.7	120.7	123.7
C2–C3	1.403	1.408	1.394	C2–C3–C4	124.3	121.3	124.5
C3–C4	1.390	1.395	1.396	C3-C4–C5	117.4	119.9	116.7
C4–C5	1.378	1.397	1.366	C4-C5–C6	122.7	119.8	123.3
C5–C6	1.389	1.396	1.372	C5-C6-C7	116.4	119.9	116.7
C6–C7	1.382	1.396	1.379	C6–C7–C2	125.7	121.3	125.2
C7–C2	1.399	1.405	1.394	C7-C2-C3	113.6	117.7	113.4
C3-N1	1.475	1.516	1.470	C2-C3-N1	119.6	121.8	119.9
C5-N2	1.475	1.510	1.483	C4-C3-N1	116.1	116.9	115.6
C7-N3	1.475	1.517	1.485	C2-C7-N3	118.9	121.8	118.6
$(N–O)_{ave}$	1.225(6)	1.211	1.218(9)	C6-C7-N3	115.6	116.9	116.1
				C4-C5-N2	119.0	119.1	118.0
				C6–C5-N2	118.3	120.1	118.7
				$(C–N–O)_{ave}$	117.5(6)	118.5	117.5(9)
				$(O–N–O)_{ave}$	125.0(3)	123.0	124.9(3)

*Atom designations as in Ref. [4].

Table 2. Bond distances (Å) and bond angles (degrees) for form B TNT and TNT-d_3

	TNT		TNT-d_3		TNT		TNT-d_3
Distance*	Obs.	Calc.	Obs.	Angle	Obs.	Calc.	Obs.
C8–C9	1.494	1.487	1.492	C8-C9–C10	124.4	120.7	124.9
C9–C10	1.404	1.408	1.397	C9–C10–C11	124.7	121.3	125.1
C10–C11	1.380	1.395	1.379	C10–C11–C12	117.4	119.9	117.0
C11–C12	1.381	1.397	1.390	C11–C12–C13	122.8	119.8	123.0
C12–C13	1.379	1.396	1.376	C12–C13–C14	116.1	119.9	115.9
C13–C14	1.375	1.396	1.386	C13–C14–C9	126.4	121.3	126.1
C14–C9	1.400	1.405	1.403	C14–C9–C10	112.6	117.7	112.9
C10–N4	1.482	1.516	1.488	C9–C10–N4	119.5	121.8	119.5
C12–N5	1.467	1.510	1.464	C11-C10–N4	115.8	116.9	115.5
C14–N6	1.486	1.517	1.474	C9–C14–N6	117.8	121.8	118.0
$(N-O)_{ave}$	1.228(4)	1.211	1.221(3)	C14–C12–N5	115.8	116.9	115.8
				C11-C12-N5	119.8	119.1	118.3
				C13-C12-N5	118.4	120.1	118.6
				$(C–N–O)_{ave}$	117.4(5)	118.5	117.3(5)
				$(O–N–O)_{ave}$	125.2(4)	123.0	125.4(8)

*Atom designation as in Ref. [4].

Table 3. Dihedral angles (degrees) between nitro groups and the plane of the ring in 2,4,6-trinitrotoluene isotopomers

Molecular form	Nitro group 2	4	6
A (Ref. [4])	51	24	43
A (this work)	52.0	22.3	43.4
A-d_3 (this work)	51.8	23.0	42.3
B (Ref. [4])	60	30	45
B (this work)	58.7	33.0	39.6
B-d_3 (this work)	58.9	33.0	39.5
Calc. (this work)	55.1	9.3	76.2

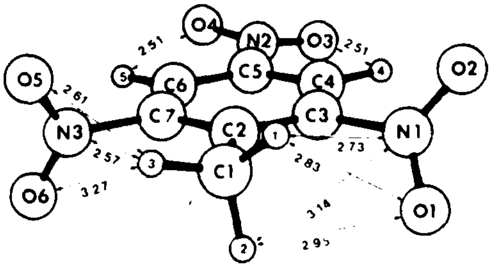

Fig. 1. Calculated molecular structure of 2,4,6-trinitrotoluene. The atom designation is that of TNT structure A in Ref. [4], and distances are in Å.

work. We observe O · · · H hydrogen contacts between two A molecules (O5 H2) and an A and a B molecule (O4 H10) that approximate distances of 2.5 Å. Only the first of these involves the kind of methyl-hydrogen-to-nitro-oxygen interaction that has been implicated in the thermal degradation of TNT. Of greater significance is the complete lack of hydrogen bonding involving the *para*-nitro groups. Such absences are consistent with the *para*-nitro group being unreactive in the thermal or ionization breakdown of TNT [14–16].

Tables 4 and 5 contain the calculated [5, 6] and observed [1, 3] vibration frequencies of TNT and TNT-d_3. The symmetry designations [1] are based on the nominal C_{2v} symmetry of the calculated structure, with the principal axis in the z-direction and the y-direction orthogonal to the plane of the ring. The A_2 and B_1 vibrations are out-of-plane; A_2 vibrations are i.r. inactive if the molecule has genuine C_{2v} symmetry, but such is not the case in the present instance and at least some of the A_2-species vibrations may become observable.

In correlating calculated vibrational frequencies to those observed, emphasis was placed on absorption intensities and isotopic substitution [3]. In the majority of cases, calculated absorption frequencies with large transition dipoles were identified with the more intense absorption bands. The major improvement in the calculations occurs in the NO_2 ν_{sym} and ν_{asym} stretching frequencies, where the error compared to previous calculations [3] decreases from 34% to 22%. The C–H stretching frequencies in the 2800–3100 cm^{-1} range are reproduced with an average error of 1.3% vs 3.0% using the AM1 method. The remaining frequencies over the range of 400–1800 cm^{-1} are reproduced with an average error

Table 4. Observed and calculated frequencies (cm^{-1}) for 2,4,6-trinitrotoluene

ν^*_{obs}					Transition
KBr	Vapour	ν_{calc}	Symmetry	Assignment†	dipole
465		444	B_1, B_2	11, 14	0.10
467		480	B_2	12	0.28
565		533	B_1	12	0.34
579		558	B_2	15	0.21
639		634	A_2	5, 12	1.40
664		669	A_1	17	2.37
664		673	A_1	17	2.10
704, 720	705, 721	743	A_2	17	0.78
		745	A_2	15	0.06
735	730	749	B_1	15	0.56
793	792	769	B_2	15	1.15
		805	B_1	15	0.13
-	868	849	A_1	12	1.21
909, 940	907, 936	939	B_2	16	1.32
		971	A_2	13	0.11
		990	B_1	6	0.10
		995	A_1	16	1.93
1026	1028, 1067	1032	B_1	12, 13	0.30
1086	1075	1049	B_2	4, 6	0.75
1171		1182	A_1	10	0.40
1208	1217, 1230	1247	B_2	10, 12	0.12
		1271	A_1	12	0.05
		1334	B_2	9	0.19
		1360	A_1	4	0.15
1356	1352	1581	A_1	19	5.90
1356	1352	1589	B_2	19	5.90
1356	1352	1604	A_1	19	0.80
		1376	B_2	4	0.09
1406	1420	1414	A_1	9, 16	0.62
1437, 1466	1437, 1457	1449	A_1	7, 11	0.28
		1551	B_2	9	1.43
1541	1508	1918	A_2	18	3.51
1541	1539	1921	B_2	18	7.58
1541	1539	1925	B_2	18	7.26
1603, 1619	1617	1614	A_1	8, 9	1.12
	1734	1770	B_2	9	1.19
		1790	A_1	9	2.67
2955	2901	2983	B_2	1	0.50
3015	2971	2991	A_1	1	0.42
3058	2991	3057	B_2	2	0.25
3087	3085	3070	A_1	2	0.18
3096	3096	3176	A_1	3	0.30

*Data from Ref. [1, 3].

†Assignments of vibrational frequencies: 1. Ring C–H stretch; 2. Methyl C–H asym. stretch; 3. Methyl C–H sym. stretch; 4. Methyl H–C–H asym. bend; 5. Methyl H–C–H sym. bend; 6. Methyl rock; 7. Methyl umbrella; 8. C–C stretch: methyl to ring; 9. C–C ring stretch; 10. Ring H–C–C in plane bend; 11. Methyl ring CCC in-plane bend; 12. Ring CCC bend; 13. Out-of-plane bend of ring H; 14. Out-of-plane bend of methyl C; 15. C–N bend; 16. C–N stretch; 17. C–N–O bend; 18. NO_2 asym. stretch; 19. NO_2 sym. stretch.

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Table 5. Observed and calculated frequencies (cm^{-1}) for 2,4,6-trinitrotoluene-α-d_3

ν^*_{obs} KBr	Vapour	ν_{calc}	Symmetry	Assignment†	Transition dipole
457, 471		465	B_1	12	0.30
563	—	527	B_1	12	0.29
573	—	554	B_2	15	0.20
625	—	623	A_1	5, 15	1.28
677	—	666	B_2	15	1.65
677		672	B_1	15	2.35
718	718	694	A_2, B_2	4	0.41
733	731	730	A_2	17	0.68
—	749	743	A_1	17	0.86
758	758	749	A_2	15	0.65
775	778	769	B_1	15	0.84
826	826	804	A_1	15	0.84
826	826	819	B_2	15	0.79
872, 909	907	894	B_1	12	0.19
938	938	971	A_2	13	0.13
938	938	982	B_2	16	2.51
938	938	989	A_1	16	2.49
1030		1009	B_1	13	0.23
1030		1017	B_1	13	0.31
1030		1025	B_1	4	0.35
1057, 1095	1057, 1067	1070	A_1	7	0.09
1179, 1198		1186	A_1	10	0.40
1219, 1264	1254	1245	B_2	10	0.14
1302		1307	A_1	8	0.17
—	—	1333	B_2	9	0.18
1354	1352	1581	A_1	19	5.89
1354	1352	1589	B_2	19	5.91
1354	1352	1604	A_1	19	0.85
1410		1418	A_1	9, 16	1.06
1539	1508	1918	A_2	18	3.50
1541	1539	1921	B_2	18	7.61
1541	1539	1925	B_2	18	7.23
1599		1550	B_2	9	1.46
1619		1613	A_1	8, 9	1.13
—		1768	B_2	9	1.21
		1790	A_1	19	2.67
	2275	2258	B_1	2	0.38
	2325	2273	B_2	2	0.22
	2325	2293	A_1	3	0.26
3058	2907	2983	B_2	1	0.50
3096, 3087	2971	2991	A_1	1	0.42

*Data from Refs [1, 3].
†Assignments of vibrational frequencies. See Table 4.

of less than 21 cm^{-1}, down slightly from the 24 cm^{-1} with the AM1 method [3].*

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