Structure of 1-Amino-3,5,7-trinitroadamantane

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Abstract. $C_{10}H_{14}N_4O_6$, $M_r = 572.5$, monoclinic, $P2_1/n$, $a = 14.089$, $b = 13.806$ (3), $c = 14.414$ (3) Å, $\beta = 118.86$ (2)°, $V = 2455.5$ (9) Å^3, $Z = 8$, $D_x = 1.55$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54184 Å, $\mu = 1.1$ mm^{-1}, $F(000) = 1200$, $T = 295$ K, final $R = 0.058$, $wR = 0.065$ for 2600 independent observed reflections. There are two molecules in the asymmetric unit which differ primarily in the relative orientation of the nitro groups to the adamantane cage.

Introduction. There is considerable interest in the synthesis of polynitropolycyclic cage molecules because of their potential energetic properties (Marchand, 1988). Oxidation of a primary amine to a nitro group is the most common way of introducing a nitro group into a cage compound. We have recently developed methods by which this transformation can be achieved using inexpensive and easy-to-handle oxidizing systems (Zajac, Walters & Woods, 1988; Zajac, Darcy, Subong & Buzby 1989). When the sodium percarbonate–tetraacetylethylenediamine oxidizing system was used to oxidize 1,3,5,7-tetraaminoadamantane, the product isolated was not the expected 1,3,5,7-tetranitrosoadamantane but rather a product to which the 1-amino-3,5,7-trinitroadamantane structure was assigned based on spectroscopic analysis (Zajac, Walters & Woods, 1989). The X-ray analysis of this compound was undertaken to determine definitively the structure of this unusual oxidation product. Furthermore, the structural parameters provided could be helpful in explaining the unusual subsequent oxidation of this compound to 1,3,5,7-tetranitroadamantane.

Experimental. A clear colorless plate of dimensions $0.08 \times 0.25 \times 0.40$ mm was used for data collection on an automated Siemens $R3m/V$ diffractometer with incident-beam graphite-monochromatized Cu $K\alpha$ radiation. 25 centered reflections within $35 \leq 2\theta \leq 82°$ were used for determining the lattice parameters. θ–2θ scans. Data were collected to

$[\sin(\theta)/\lambda]_{max} = 0.50$ Å^{-1}, covering the range $0 \leq h \leq 15$, $0 \leq k \leq 14$, $-15 \leq l \leq 13$. The standards (400, 060, 004) were monitored every 60 reflections and showed a random variation of 2.5% over data collection. In the $\theta/2\theta$ scan mode the scan width was $[2\theta(K\alpha_1) - 1.0]$ to $[2\theta(K\alpha_2) + 1.0]°$; the ω scan rate was a function of count rate (5.0° min^{-1} minimum, 15.0° min^{-1} maximum). 3661 reflections were measured with 3213 unique, $R_{int} = 0.9\%$, 2600 observed with $F_o > 3\sigma(F_o)$. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods, and the full-matrix least-squares refinement used programs in *SHELXTL* (Sheldrick, 1980). $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$, $g = 0.000225$. Secondary-extinction parameter $p = 0.0015$ (3) in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. 412 parameters were refined: atomic coordinates and anisotropic thermal parameters for all non-H atoms, H atoms included using riding model [coordinate shifts of C applied to attached H atoms, C—H distance set to 0.96 Å, H-atom angles idealized, U_{iso}(H) set to $1.1U_{eq}$(C)], ratio of observations to parameters 6.3:1, $R = 0.058$, $wR = 0.065$, $S = 2.15$, $R = 0.071$ for all data. Final difference Fourier excursions 0.27 and -0.23 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).* Table 1 lists atomic coordinates and displacement parameters, Table 2 bond lengths and angles and Fig. 1 shows a thermal ellipsoid plot with the atom-numbering scheme.

Discussion. Both of the unique molecules present in the asymmetric unit are shown in Fig. 1. The most significant difference between the two is the orientation of the nitro groups at C(3) and C(3′) and the

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	6560 (3)	3420 (2)	1554 (3)	41 (2)
N(1)	6450 (3)	4473 (2)	1383 (3)	58 (2)
C(2)	5697 (3)	2854 (2)	609 (3)	43 (2)
C(3)	5876 (3)	1770 (3)	845 (3)	43 (2)
N(3)	4995 (3)	1247 (2)	−122 (3)	63 (3)
O(3A)	4128 (3)	1151 (3)	−205 (3)	115 (2)
O(3B)	5196 (3)	977 (3)	−793 (3)	122 (2)
C(4)	6976 (3)	1468 (3)	997 (3)	49 (3)
C(5)	7820 (3)	2037 (3)	1947 (3)	45 (2)
N(5)	8946 (3)	1755 (3)	2135 (3)	71 (2)
O(5A)	9714 (8)	2116 (12)	2878 (10)	93 (5)
O(5B)	9030 (7)	1092 (18)	1634 (11)	132 (8)
O(5C)	9115 (9)	1880 (21)	1378 (9)	95 (7)
O(5D)	9630 (20)	1534 (31)	2997 (18)	143 (12)
C(6)	7747 (3)	1792 (3)	2941 (3)	47 (2)
C(7)	6630 (3)	2090 (2)	2740 (3)	42 (2)
N(7)	6506 (3)	1855 (3)	3708 (3)	63 (2)
O(7A)	5621 (3)	1967 (2)	3639 (3)	87 (2)
O(7B)	7288 (3)	1576 (3)	4490 (3)	105 (2)
C(8)	6465 (3)	3180 (2)	2537 (3)	46 (2)
C(9)	7678 (3)	3118 (3)	1735 (3)	49 (2)
C(10)	5755 (3)	1525 (3)	1806 (3)	48 (2)
C(1')	8006 (3)	1575 (3)	8201 (3)	51 (2)
N(1')	8439 (3)	2542 (3)	8626 (3)	68 (2)
C(2')	8449 (3)	1269 (3)	7459 (3)	50 (2)
C(3')	7967 (3)	290 (3)	6985 (3)	43 (2)
N(3')	8395 (3)	−44 (3)	6242 (3)	62 (2)
O(3'A)	7987 (3)	−771 (3)	5716 (3)	95 (2)
O(3'B)	9111 (3)	400 (3)	6214 (3)	94 (2)
C(4')	8297 (3)	−485 (3)	7836 (3)	50 (2)
C(5')	7851 (3)	−170 (3)	8570 (3)	46 (2)
N(5')	8178 (4)	−919 (4)	9446 (3)	75 (2)
O(5'A)	8840 (10)	−1509 (8)	9540 (01)	106 (8)
O(5'B)	7878 (15)	−791 (10)	10049 (11)	144 (14)
O(5'C)	8916 (9)	−825 (9)	10269 (9)	154 (7)
O(5'D)	7565 (9)	−1632 (7)	9253 (8)	157 (7)
C(6')	6621 (3)	−112 (3)	7955 (3)	48 (2)
C(7')	6323 (3)	651 (3)	7098 (3)	41 (2)
N(7')	5094 (3)	750 (3)	6456 (3)	54 (2)
O(7'A)	4530 (3)	281 (3)	6691 (3)	100 (2)
O(7'B)	4732 (3)	1305 (3)	5732 (3)	111 (2)
C(8')	6776 (3)	1638 (3)	7581 (3)	48 (2)
C(9')	8333 (3)	804 (3)	9073 (3)	55 (2)
C(10')	6736 (3)	355 (3)	6336 (3)	47 (2)

Table 2. Bond lengths ($\mathring{A}$) and bond angles ($°$)

C(1)—N(1)	1·470 (5)	C(1)—C(2)	1·531 (4)
C(1)—C(8)	1·522 (6)	C(1)—C(9)	1·526 (6)
C(2)—C(3)	1·529 (5)	C(3)—N(3)	1·528 (4)
C(3)—C(4)	1·517 (6)	C(3)—C(10)	1·513 (6)
N(3)—O(3A)	1·175 (7)	N(3)—O(3B)	1·191 (7)
C(4)—C(5)	1·528 (4)	C(5)—N(5)	1·525 (6)
C(5)—C(6)	1·523 (6)	C(5)—C(9)	1·517 (5)
N(5)—O(5A)	1·203 (11)	N(5)—O(5B)	1·207 (23)
N(5)—O(5C)	1·237 (16)	N(5)—O(5D)	1·188 (22)
C(6)—C(7)	1·514 (6)	C(7)—N(7)	1·523 (7)
C(7)—C(8)	1·530 (5)	C(7)—C(10)	1·529 (4)
N(7)—O(7A)	1·211 (7)	N(7)—O(7B)	1·198 (4)
C(1')—N(1')	1·473 (5)	C(1')—C(2')	1·535 (7)
C(1')—C(8')	1·521 (5)	C(1')—C(9')	1·538 (5)
C(2')—C(3')	1·519 (5)	C(3')—N(3')	1·532 (6)
C(3')—C(4')	1·522 (5)	C(3')—C(10')	1·525 (5)
N(3')—O(3'A)	1·221 (5)	N(3')—O(3'B)	1·198 (6)
C(4')—C(5')	1·531 (7)	C(5')—N(5')	1·521 (6)
C(5')—C(6')	1·521 (5)	C(5')—C(9')	1·522 (5)
N(5')—O(5'A)	1·196 (15)	N(5')—O(5'B)	1·149 (22)
N(5')—O(5'C)	1·147 (10)	N(5')—O(5'D)	1·248 (12)
C(6')—C(7')	1·521 (5)	C(7')—N(7')	1·525 (5)
C(7')—C(8')	1·524 (5)	C(7')—C(10')	1·525 (6)
N(7')—O(7'A)	1·194 (6)	N(7')—O(7'B)	1·193 (5)

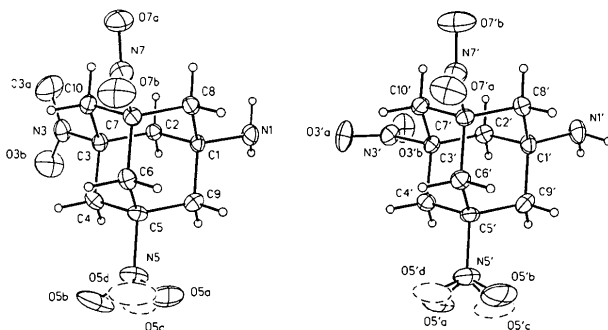| | | | | |
|---|---|---|---|
| N(1)—C(1)—C(2) | 112·4 (2) | N(1)—C(1)—C(8) | 108·8 (3) |
| C(2)—C(1)—C(8) | 109·2 (3) | N(1)—C(1)—C(9) | 108·3 (3) |
| C(2)—C(1)—C(9) | 108·9 (3) | C(8)—C(1)—C(9) | 109·2 (3) |
| C(1)—C(2)—C(3) | 109·1 (2) | C(2)—C(3)—N(3) | 106·6 (2) |
| C(2)—C(3)—C(4) | 110·4 (3) | N(3)—C(3)—C(4) | 109·0 (3) |
| C(2)—C(3)—C(10) | 110·1 (3) | N(3)—C(3)—C(10) | 109·2 (3) |
| C(4)—C(3)—C(10) | 111·4 (3) | C(3)—N(3)—O(3A) | 119·5 (4) |
| C(3)—N(3)—O(3B) | 118·8 (4) | O(3A)—N(3)—O(3B) | 121·7 (4) |
| C(3)—C(4)—C(5) | 106·6 (3) | C(4)—C(5)—N(5) | 108·7 (3) |
| C(4)—C(5)—C(6) | 110·6 (3) | N(5)—C(5)—C(6) | 108·2 (3) |
| C(4)—C(5)—C(9) | 110·8 (3) | N(5)—C(5)—C(9) | 108·2 (3) |
| C(6)—C(5)—C(9) | 110·2 (3) | C(5)—N(5)—O(5A) | 117·6 (8) |
| C(5)—N(5)—O(5B) | 118·7 (5) | O(5A)—N(5)—O(5B) | 122·8 (9) |
| C(5)—N(5)—O(5C) | 115·7 (7) | C(5)—N(5)—O(5D) | 120·1 (17) |
| O(5C)—N(5)—O(5D) | 123·7 (17) | C(5)—C(6)—C(7) | 107·2 (3) |
| C(6)—C(7)—N(7) | 109·6 (3) | C(6)—C(7)—C(8) | 110·6 (3) |
| N(7)—C(7)—C(8) | 108·1 (3) | C(6)—C(7)—C(10) | 110·6 (3) |
| N(7)—C(7)—C(10) | 107·3 (3) | C(8)—C(7)—C(10) | 110·5 (2) |
| C(7)—N(7)—O(7A) | 117·8 (3) | C(7)—N(7)—O(7B) | 118·1 (5) |
| O(7A)—N(7)—O(7B) | 124·1 (5) | C(1)—C(8)—C(7) | 108·5 (3) |
| C(1)—C(9)—C(5) | 109·1 (3) | C(3)—C(10)—C(7) | 107·0 (3) |
| N(1')—C(1')—C(2') | 108·3 (4) | N(1')—C(1')—C(8') | 108·6 (3) |
| C(2')—C(1')—C(8') | 109·7 (3) | N(1')—C(1')—C(9') | 112·8 (3) |
| C(2')—C(1')—C(9') | 108·4 (3) | C(8')—C(1')—C(9') | 109·1 (4) |
| C(1')—C(2')—C(3') | 108·3 (4) | C(2')—C(3')—N(3') | 110·0 (4) |
| C(2')—C(3')—C(4') | 111·5 (3) | N(3')—C(3')—C(4') | 106·4 (3) |
| C(2')—C(3')—C(10') | 110·6 (3) | N(3')—C(3')—C(10') | 107·7 (3) |
| C(4')—C(3')—C(10') | 110·5 (3) | C(3')—N(3')—O(3'A) | 117·1 (4) |
| C(3')—N(3')—O(3'B) | 119·4 (4) | O(3'A)—N(3')—O(3'B) | 123·5 (5) |
| C(3')—C(4')—C(5') | 106·9 (3) | C(4')—C(5')—N(5') | 108·6 (4) |
| C(4')—C(5')—C(6') | 110·1 (3) | N(5')—C(5')—C(6') | 108·8 (4) |
| C(4')—C(5')—C(9') | 110·0 (4) | N(5')—C(5')—C(9') | 108·6 (3) |
| C(6')—C(5')—C(9') | 110·7 (3) | C(5')—N(5')—O(5'A) | 117·6 (9) |
| C(5')—N(5')—O(5'B) | 116·7 (8) | O(5'A)—N(5')—O(5'B) | 124·8 (11) |
| C(5')—N(5')—O(5'C) | 122·8 (8) | C(5')—N(5')—O(5'D) | 116·8 (5) |
| O(5'C)—N(5')—O(5'D) | 120·3 (9) | C(5')—C(6')—C(7') | 107·4 (3) |
| C(6')—C(7')—N(7') | 110·0 (3) | C(6')—C(7')—C(8') | 111·0 (3) |
| N(7')—C(7')—C(8') | 107·4 (3) | C(6')—C(7')—C(10') | 110·4 (3) |
| N(7')—C(7')—C(10') | 107·7 (3) | C(8')—C(7')—C(10') | 110·3 (3) |
| C(7')—N(7')—O(7'A) | 119·7 (3) | C(7')—N(7')—O(7'B) | 118·0 (4) |
| O(7'A)—N(7')—O(7'B) | 122·3 (4) | C(1')—C(8')—C(7') | 109·0 (3) |
| C(1')—C(9')—C(5') | 109·5 (3) | C(3')—C(10')—C(7') | 106·9 (3) |

Fig. 1. Thermal ellipsoid plot showing both molecules in the asymmetric unit viewed in a common orientation. Drawn at the 20% probability level with dotted ellipsoids representing lower occupation disordered atoms.

amines at C(1) and C(1'). The C(2)—C(3)—N(3)—O(3B) torsion angles are 94·5 (4) and 8·8 (4)°, respectively, and the Newman projection of the N—H bonds along the N(1)—C(1) bond shows a difference of 127° for the two molecules. In each molecule the N—H bonds are in a staggered configuration with respect to the C(1)—C bonds. In addition the disordered nitro groups, which are present in occupancy ratios 60:40 and 54:46, respectively, are oriented differently.

The bond distances and angles for the cage and nitro substituents are very similar to those found in 1,3,5,7-tetranitroadamantane (George & Gilardi, 1984), 2,2-dinitroadamantane and 2-bromo-2-

nitroadamantane (George & Gilardi, 1983), and are near ideal values for the cage. Bond angles for the cage atoms do show some distortion; the average angle about the tertiary carbons is 110·2 (8)°, while the average angle about the secondary carbons is 108·0 (1·2)°. The average C—C distance is 1·524 Å; in the previously cited compounds it is 1·533, 1·525 and 1·525 Å, respectively, while in the low-temperature form of adamantane (Donohue & Goodman, 1967), it is 1·536 Å.

One of the H atoms from each of the amido groups participates in a weak hydrogen bond. The hydrogen-bond parameters are $N(1)\cdots O(3'B) =$ 3·190 (7), $H(1NB)\cdots O(3'B) = 2\cdot34$ (5) Å, N—H—O = 163 (3)° and $N(1')\cdots O(7A) = 3\cdot140$ (7), $H(1NC)\cdots O(7A) = 2\cdot43$ (5) Å, N—H—O = 133 (3)°, respectively, via symmetry operations $(x - 0\cdot5, 0\cdot5 - y, z - 0\cdot5)$ and $(x + 0\cdot5, 0\cdot5 - y, z + 0\cdot5)$.

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Structure of 4-Methoxy-2,6-dimethylbenzamide

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Abstract. $C_{10}H_{13}NO_2$, $M_r = 179\cdot22$, m.p. 439–440 K, monoclinic, $P2_1/c$, $a = 5\cdot008$ (4), $b = 6\cdot624$ (3), $c = 29\cdot813$ (13) Å, $\beta = 93\cdot03$ (6)°, $V = 988$ (1) Å^3, $Z = 4$, $D_m = 1\cdot208$, $D_x = 1\cdot205$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot079$ mm^{-1}, $F(000) = 384$, $T = $ 293 K, final $R = 0\cdot052$ for 1614 independent reflections with $F > 3\sigma(F)$. The carbamoyl group is rotated by 56·7 (1)° with respect to the benzene ring plane. Molecular-orbital calculations yield dihedral angles of 72·4 and 32·3° for the isolated molecules of the title compound and of the parent 4-methoxybenzamide, respectively. In the crystal the molecules are linked in endless chains by hydrogen bonds involving the carbamoyl group.

Introduction. A recent ^{13}C NMR study (Dell'Erba, Mele, Novi, Petrillo, Sancassan & Spinelli, 1990) has shown the existence of a linear correlation between the carbonyl-carbon chemical shifts of 4-X-benzamides and 2,6-dimethyl-4-X-benzamides, in spite of an expected larger steric inhibition to conjugation between the CONH$_2$ group and the ring in

2,6-dimethyl derivatives. To confirm the latter point and to assist in the interpretation of the observed behaviour, an X-ray crystal structure determination of the title compound (1) together with molecular-orbital calculations on both (1) and the 2,6-unsubstituted derivative (2) have been performed.

Experimental. Transparent crystals were obtained from an ethyl acetate solution. A prismatic crystal of dimensions 0·38 × 0·45 × 0·22 mm was used to collect data on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation, ω-scan mode, scan width 1·8°, scan speed 1·2–5° min^{-1}, θ range 2·5–27·5°; unit cell from 25 reflections, 16·7 < θ < 19°, least-squares refinement; max. $(\sin\theta)/\lambda = $ 0·65 Å^{-1}; 4668 reflections collected with h 0 to 6, k −8 to 8, l −38 to 38, for a total of 2275 independent reflections; two check reflections monitored every hour to test the crystal stability, and eight to test the crystal orientation; no absorption correction applied $(\mu V_s^{1/3} = 0\cdot026$; $V_s = $ volume of the crystal sample); $P2_1/c$ from systematic absences; 1614