

The observation that the bond lengths in BPM do not show major deviations from standard values in unhindered molecules renders these findings especially important. They imply that the steric strain in molecules containing Ar\* as a stabilizing substituent is relieved predominantly by a boat deformation of the phenyl rings. One may further conclude that sterically heavily congested molecules stabilized by Ar\* should be reasonable approximations of their (unstable) homologues with sterically less demanding substituents and should yield representative structural parameters (particularly bond lengths) for the novel multiple bond geometries.

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### 4,4-Dinitropentanoic Acid

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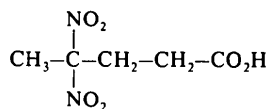
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**Abstract.** C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>, *M<sub>r</sub>* = 192.1, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 9.625 (6), *b* = 9.879 (3), *c* = 9.875 (4) Å, β = 121.25 (4)°, *V* = 802.7 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.589 Mg m<sup>-3</sup>, *Cu Kα* (λ = 1.5418 Å), μ = 1.25 mm<sup>-1</sup>, *F*(000) = 400, *T* = 295 K, 1292 unique reflections, 1088 with *I* > 3σ above background, final *R* = 0.041. Bond lengths and angles are normal. The mean deviation (magnitude) of atoms C(1), C(2), C(3) and C(4) from their least-squares plane is 0.048 Å. The carboxyl group and the two nitro groups in the molecule are twisted out of this plane by 8.9, 74.9 and 75.9°, respectively. The two C–N bond distances are

identical [1.539 (2) Å] and the four N–O distances of the nitro groups are within 0.005 Å of their mean value of 1.214 Å. The molecules form tight H-bonded dimers [H⋯O = 1.71 (3) Å] across centers of symmetry.

**Introduction.** We are investigating the crystal structures of a series of high-density, nitro-group-containing organic compounds as part of an overall study of the relationships between molecular structure and density in energetic materials. The title compound (I) was of interest because of the dinitroalkyl moiety.



(I)

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**Experimental.** The compound was obtained from Dr H. Adolph, Naval Surface Weapons Center, Silver Spring, Maryland, and crystallized from acetone/water as elongated prisms. Picker FACS-I diffractometer, graphite monochromator, Cu  $K\alpha$  radiation,  $0.3 \times 0.2 \times 0.15$  mm crystal,  $2\theta$  values of 12 reflections automatically centered at  $\pm 2\theta$  and used to obtain accurate cell parameters by least squares.  $\theta$ - $2\theta$  scan,  $2^\circ \text{ min}^{-1}$ , 10 s background, scan with  $1.35 + 0.29^\circ \tan \theta$ . Maximum and minimum  $h, k, l$  of 11, 11, 9 and 0, 0, -9. Maximum  $2\theta = 126^\circ$ . Four standard reflections (312,  $41\bar{3}$ ,  $33\bar{3}$ ,  $\bar{2}53$ ) measured every 65 reflections with average and maximum intensity deviations of 1.2 and 4.2%, 1292 reflections measured, 1088  $3\sigma$  above background. Structure solved with the direct-methods program *MULTAN80* (Main *et al.*, 1980), H atoms located from a difference map, full-matrix least-squares structure refinement, anisotropic temperature factors for C, N and O, individual isotropic terms for H,  $\sum w(F_o - F_c)^2$  minimized,  $w = [1/\sigma(F)]^2$ , reflections with  $I_o < 3\sigma(I)$  not included in refinement. Maximum and average shift/e.s.d. of 0.29 [for  $z$  of O(2)] and 0.11 in final least-squares cycle. Maximum and minimum heights in final difference map 0.14 and  $-0.22 \text{ e } \text{\AA}^{-3}$ . C, N and O scattering factors from Cromer & Mann (1968), H from Stewart, Davidson & Simpson (1965), final  $R, wR$  and  $S$  are 0.041, 0.044 and 2.31. Univac 1100/82 computer at University of Maryland Computer Science Center, *XRAY76* system of crystallographic programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

**Discussion.** Atomic coordinates and thermal parameters are listed in Table 1.\* An *ORTEP* drawing of the molecule is shown in Fig. 1. Bond lengths, bond angles and dihedral angles are listed in Table 2. The lengths and angles have normal values. The four central atoms C(1), C(2), C(3), C(4) of the carbon chain are nearly planar (plane *A*) with a maximum deviation of  $0.052 \text{ \AA}$  for C(3). Atoms N(1) and N(2) deviate from this plane by  $1.272$  and  $-0.154 \text{ \AA}$ , respectively. Atom N(2) is thus nearly in plane *A*. The angles between plane *A* and the planes of the carboxyl and the two nitro groups are  $8.9$ ,  $74.9$  and  $75.9^\circ$ , respectively. The twist of nitro group N(2), O(5), O(6) around the C(4)-N(2) bond brings O(6) closer to the nitrogen atom N(1) of the second nitro group [ $\text{O}(6) \cdots \text{N}(1) = 2.560(3) \text{ \AA}$ ]. Such short  $\text{O} \cdots \text{N}$  contacts have been observed in several nitro compounds by Bhattacharjee & Ammon (1982). They have suggested that the observed short

\* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42915 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and isotropic temperature factors ( $\text{\AA}^2$ ) with their e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$U_{eq}$
C(1)	0.0129 (2)	-0.3457 (2)	0.3866 (2)	0.043 (4)
C(2)	0.0110 (2)	-0.2246 (2)	0.2934 (2)	0.038 (2)
C(3)	0.1366 (3)	-0.1201 (2)	0.4001 (2)	0.040 (3)
C(4)	0.1266 (2)	0.0134 (2)	0.3189 (2)	0.041 (4)
C(5)	-0.0356 (3)	0.0837 (2)	0.2328 (3)	0.066 (4)
O(1)	0.0924 (2)	-0.3525 (1)	0.5304 (2)	0.043 (2)
O(2)	-0.0825 (2)	-0.4435 (1)	0.2952 (2)	0.039 (1)
O(3)	0.2586 (2)	-0.1057 (2)	0.2090 (2)	0.116 (3)
O(4)	0.1660 (2)	0.0930 (2)	0.1167 (2)	0.089 (3)
O(5)	0.2103 (2)	0.1560 (2)	0.5370 (2)	0.064 (4)
O(6)	0.3839 (2)	0.1221 (2)	0.4644 (2)	0.047 (4)
N(1)	0.1906 (2)	-0.0017 (2)	0.2057 (2)	0.046 (2)
N(2)	0.2521 (2)	0.1066 (2)	0.4506 (2)	0.044 (1)

Table 2. Bond lengths ( $\text{\AA}$ ), angles ( $^\circ$ ) and dihedral angles ( $^\circ$ ) with their e.s.d.'s in parentheses

C(1)-C(2)	1.504 (3)	C(4)-N(1)	1.539 (4)
C(1)-O(1)	1.216 (3)	C(4)-N(2)	1.539 (2)
C(1)-O(2)	1.316 (2)	N(1)-O(3)	1.209 (3)
C(2)-C(3)	1.522 (3)	N(1)-O(4)	1.219 (3)
C(3)-C(4)	1.520 (3)	N(2)-O(5)	1.217 (3)
C(4)-C(5)	1.505 (3)	N(2)-O(6)	1.213 (3)
C(2)-C(1)-O(1)	124.0 (2)	C(5)-C(4)-N(2)	109.3 (2)
C(2)-C(1)-O(2)	112.4 (2)	N(1)-C(4)-N(2)	103.7 (2)
O(1)-C(1)-O(2)	123.6 (2)	C(4)-N(1)-O(3)	118.5 (2)
C(1)-C(2)-C(3)	111.2 (2)	C(4)-N(1)-O(4)	116.6 (2)
C(2)-C(3)-C(4)	114.4 (2)	O(3)-N(1)-O(4)	124.9 (3)
C(3)-C(4)-C(5)	117.5 (2)	C(4)-N(2)-O(5)	115.6 (2)
C(3)-C(4)-N(1)	111.1 (2)	C(4)-N(2)-O(6)	119.1 (2)
C(3)-C(4)-N(2)	105.4 (2)	O(5)-N(2)-O(6)	125.2 (2)
C(5)-C(4)-N(1)	108.8 (2)		
C(1)-C(2)-C(3)-C(4)	-172.0 (2)		
C(2)-C(3)-C(4)-N(1)	-73.3 (2)		
C(2)-C(3)-C(4)-N(2)	175.0 (2)		
C(2)-C(3)-C(4)-C(5)	53.0 (3)		
C(3)-C(4)-N(1)-O(3)	-9.5 (2)		
C(3)-C(4)-N(1)-O(4)	169.3 (2)		
C(3)-C(4)-N(2)-O(5)	-77.8 (2)		
C(3)-C(4)-N(2)-O(6)	99.8 (2)		
C(3)-C(2)-C(1)-O(1)	7.2 (4)		
C(3)-C(2)-C(1)-O(2)	-173.4 (2)		

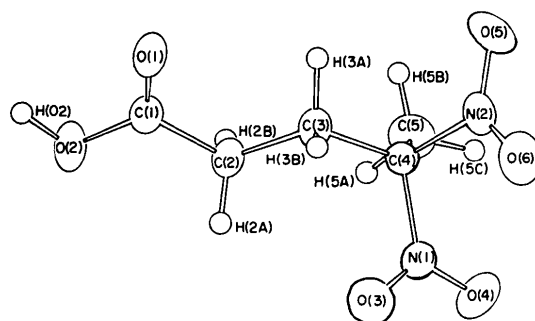


Fig. 1. An *ORTEP* drawing (Johnson, 1965) of (I) with the C, N, O atoms depicted as 50% probability boundary ellipsoids. H atoms are shown as  $0.1 \text{ \AA}$  radius circles.

O...N distances reflect a substantial attractive interaction with a large negative charge on O and a positive charge on N giving rise to a Coulombic attraction between the atoms.

The carboxyl groups form H-bonded dimers across centers of symmetry. The intermolecular distances in these dimers are O(2)...O(1) (at  $-x, -1-y, 1-z$ ) of 2.684 (2) Å, and H...O(1) of 1.71 (3) Å. There are no other significant nonbonded contacts.

The only other structure with the CH<sub>3</sub>-C(NO<sub>2</sub>)<sub>2</sub>- fragment which has come to the notice of the authors at the time of reporting this structure is 2-chloro-5,5-dinitro-3-aza-4-oxa-2-hexene [(II) (Grigor'eva *et al.*, 1975)] at  $R = 0.15$ . The present investigation gives a more precise geometry of this molecular fragment, although basically it is very similar to that in (II). The six tetrahedral angles at C(4) have a range of 103.7 (2) to 117.5 (2)° with an average of 109.3 (2)°. In (II) C(3) is replaced by an O atom, and only two angles at C(4) differ significantly, C(3)-C(4)-C(5) 117.5 (2) and C(3)-C(4)-N(2) 105.4 (2)°, the corresponding angles in (II) being 109 and 112°. The other four tetrahedral angles are nearly equal in the two structures. The nitro group N(1)-O(3)-O(4) makes a small angle of 10.2° with the plane of C(3), C(4), N(1); the other nitro group N(2), O(5), O(6) makes an angle of 15.9° with the plane of N(1)-C(4)-N(2). The corresponding angles in (II) are 5 and 9°. A comparison of the eight non-H atoms of the common fragment CH<sub>3</sub>-

C(NO<sub>2</sub>)<sub>2</sub>- in structures (I) and (II) with Nyburg's (1974) molecule-fitting program gave an r.m.s. deviation of 0.138 Å.

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## Hexadecyltrimethylammonium Bromide

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**Abstract.** [N(CH<sub>3</sub>)<sub>3</sub>(C<sub>16</sub>H<sub>33</sub>)]Br,  $M_r = 364.5$ , monoclinic,  $P2_1/c$ ,  $a = 5.638$  (1),  $b = 7.260$  (2),  $c = 52.072$  (7) Å,  $\beta = 93.78$  (1)°,  $V = 2128.8$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.14$  (2),  $D_x = 1.14$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 2.80$  mm<sup>-1</sup>,  $F(000) = 792$ ,  $T = 298$  K,  $R = 0.07$ , and  $wR = 0.07$ , for 2205 observed reflections with  $I \geq 2\sigma(I)$ . The methylenic groups of the hexadecyltrimethylammonium cation are in a fully extended conformation. The bromide ions are embedded within pockets, giving rise to van der Waals

contacts, less than 4 Å, with six methyl and two methylenic groups and to Coulombic interactions with the trimethylammonium polar heads. No water molecules were detected. The cations have an anti-parallel arrangement within a bilayer. The chain axis forms a tilt angle of 65° with the plane containing the nitrogens of the polar heads.

**Introduction.** Hexadecyltrimethylammonium bromide (CTAB) is one of the most studied cationic surfactants