

C(13), C(15), C(16); the substituents lie further out of this plane, C(17) by 0.37, C(10) by 0.22, C(25) by 0.21 Å. Similar but smaller effects are observed for the ring C(3–8). The ring C(19–24) is planar with an r.m.s. deviation of 0.004 Å.

Compound (2) crystallizes with three independent molecules in the asymmetric unit, one of which is shown in Fig. 2. The expected *endo* geometry is confirmed. The three molecules differ in the conformation of the seven-membered ring, with torsion angles about C(6)—C(9), C(9)—C(10) and C(10)—C(11) of 58, –13 and –39° for molecule 1, 44, 8 and –54° for molecule 2 and 33, 20 and –60° for molecule 3. A least-squares fit of molecule 2 to molecule 1 [except for C(9), C(10), C(20), C(21), C(23), C(24)] gave an r.m.s. deviation of 0.04 Å, and a fit of molecule 3 to molecule 1 [inverted, O(1) also omitted] gave 0.06 Å r.m.s. deviation. The bridgehead-atom deviations in the methano-bridged rings are smaller than in (1), only one of 12 values being > 0.04 Å, and are thus scarcely significant. Other features are similar to those of (1). A hydrogen bond of 2.97 Å is formed between O(1) of molecules 1 and 2. No further short contacts are observed. The molecular packing involves layers of molecules parallel to the *yz* plane and is shown in Fig. 3.

Compound (3), in contrast to (1) and (2), has only one independent molecule per asymmetric unit (Fig. 4). The expected *endo* geometry is again confirmed. The conformation is similar to that of molecule 2 of

compound (2), with smaller deviations from mirror symmetry. The torsion angles about C(6)—C(9), C(9)—C(10) and C(10)—C(11) are –49, 0 and 50°, respectively. An inverted fit of all atoms gave an r.m.s. deviation of 0.09 Å, the major deviations arising from a small rotation of the ring C(11–16). Bridgehead-atom deviations are 0.03 Å or less. The molecules are linked by weak hydrogen bonds (O...O 3.09 Å) across the threefold axes (symmetry operator: $-x + y, -x, z$). The molecular packing is shown in Fig. 5.

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Structure of Ethylenediammonium 3,5-Dinitrobenzoate

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Abstract. $0.5\text{C}_2\text{H}_{10}\text{N}_2^+\cdot\text{C}_7\text{H}_3\text{N}_2\text{O}_6^-$, $M_r = 242.17$, triclinic, $P\bar{1}$, $a = 6.737$ (1), $b = 7.803$ (7), $c = 10.444$ (1) Å, $\alpha = 94.767$ (8), $\beta = 108.30$ (1), $\gamma = 97.43$ (1)°, $V = 512.4$ (2) Å³, $Z = 2$, $D_x =$

1.570 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 1.282$ cm⁻¹, $F(000) = 250$, room temperature, $R = 0.046$, $wR = 0.054$ for 2396 observed reflections with $F_o \geq 5.0\sigma(F_o)$. The molecular complex in the lattice is extensively bonded through intermolecular and intramolecular hydrogen bonds with at least one O atom of each dinitrobenzoate substituent and each H

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atom of the ethylenediamine molecule hydrogen bonded through short (N—H...O 2.66–2.70 Å) and long (C—H...O 3.27–3.47 Å) bonds: the shortest are the N—H...O(COOH) hydrogen bonds and the longest are the C—H...O(NO₂) interactions. The molecules are stacked along the *a* and *b* axes with intermolecular distances of 3.744 (2) and 3.650 (2) Å, respectively.

Introduction. During our investigations on complexation of *s*-block cations (denoted M^{z+}) in protonic ethanol or ethanol–water medium, particularly with N-donor ligands (*G*) such as ethanalamine (ea) and ethylenediamine (en) in the presence of nitro-substituted phenolates and benzoates as charge neutralizers (L^-), we found that various ML_x-G reactions yielded $(ML)_xG$ products through metathetical reactions; the title compound is one such product obtained from the reaction of calcium 3,5-dinitrobenzoate and ethylenediamine in ethanol. Our interest in the supposed ‘proton complex’ led us to try to understand (i) how the 3,5-dinitrobenzoic proton is accepted by the neutral and coordinatively saturated ethylenediamine N atom, and (ii) the interactive chemistry of polyamines in general (Pattabhi & Chandrasekhar, 1983).

Experimental. Thin pale-green crystals of the title complex were crystallized by the slow evaporation of a calcium dinitrobenzoate/ethylenediamine (1:2) mixture in ethanol (0.1*M*) at room temperature. Using a 0.4 × 0.35 × 0.3 mm crystal, intensity data were collected on an Enraf–Nonius CAD-4 automated diffractometer with monochromated Mo *K*α radiation, $\omega/2\theta$ scan mode with ω -scan width $(0.9 + 2.70\tan\theta)^\circ$ and aperture width $(0.35 + 1.05\tan\theta)$ mm; $2\theta \leq 60^\circ$, $h\ 0 \rightarrow 9$, $k\ -11 \rightarrow 11$, $l\ -14 \rightarrow 14$ to give 3334 measured, 2987 unique and 2396 observed intensities with $F_o \geq 5.0\sigma(F_o)$. $R_{\text{int}} = 0.037$. Cell dimensions were obtained from a least-squares fit of 22 reflections, $12.7 < \theta < 21.7^\circ$. Three standard reflections ($4\bar{2}2$, 321 and $32\bar{4}$) were monitored every 100 reflections. They showed no significant variation in intensity measurements. The intensity data were corrected for Lorentz and polarization effects but not for absorption. Structure solution was by direct methods (Sheldrick, 1990) with H-atom positions from $\Delta\rho$ syntheses. Full-matrix least-squares refinement on F_o using *SHELX76* (Sheldrick, 1976) with anisotropic displacement parameters for non-H atoms and isotropic for H atoms, converged at $R = 0.046$, $wR = 0.054$, where $w = 1/[\sigma^2(F_o) + 0.0001F_o^2]$, and $(\Delta/\sigma)_{\text{max}} = 0.006$, $(\Delta/\sigma)_{\text{min}} = -0.005$, $\Delta\rho_{\text{max}} = 0.27$, $\Delta\rho_{\text{min}} = -0.297\ \text{e}\ \text{\AA}^{-3}$. $S = 1.90$ for 187 parameters. Atomic scattering factors are as given in *SHELX76*.

Discussion. The packing of the molecules is shown in Fig. 1 drawn using *PLUTO* (Motherwell & Clegg, 1978). Fractional atomic coordinates with equivalent isotropic temperature factors for non-H atoms are listed in Table 1.* Bond distances and angles for non-H atoms (with e.s.d.’s in parentheses) are shown in Table 2.

The main features of the structure are that (i) the carboxyl proton of dinitrobenzoic acid is formally transferred to the ethylenediamine N atom and (ii) dinitrobenzoate and ethylenediamine are intricately and extensively hydrogen bonded through N—H...O and C—H...O hydrogen bonds, the O atom belonging to either the carboxyl group or one of the nitro groups. The N—H...O bonds are distinctly shorter than the C—H...O bonds: the N11—H111...O61 bond is unexpectedly long [3.085 (2) Å] while the N11—H113...O21 and N11—H112...O22 bonds are short.

The O41, O61 and O22 atoms are involved in bifurcated hydrogen bonds. Observed bond lengths are in agreement with the standard values. The ethylenediamine molecule lies on the centre of inversion. The phenyl group of the dinitrobenzoate anion is almost planar and is inclined by 39.4 (1)° to the plane of the ethylenediamine molecule. The —COOH and —NO₂ groups are also rotated with

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, H-atom bond distances and angles, torsion angles and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55403 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0269]

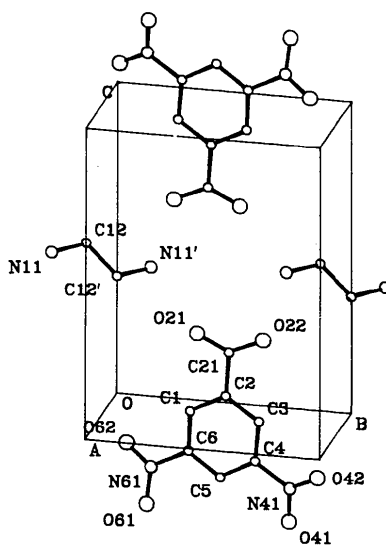


Fig. 1. Packing diagram of the molecules with the atomic numbering system.

Table 1. Atomic coordinates for the non-H atoms and equivalent isotropic temperature factors (\AA^2) with *e.s.d.*'s in parentheses
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C1	0.1936 (2)	0.3392 (2)	-0.0070 (1)	2.27 (3)
C2	0.2840 (2)	0.5038 (2)	0.0642 (1)	2.12 (3)
C21	0.3718 (2)	0.5287 (2)	0.2183 (1)	2.55 (3)
O21	0.3886 (3)	0.3947 (1)	0.2740 (1)	4.48 (4)
O22	0.4210 (3)	0.6806 (1)	0.2744 (1)	4.58 (4)
C3	0.2962 (2)	0.6467 (2)	-0.0062 (1)	2.28 (3)
C4	0.2178 (2)	0.6203 (2)	-0.1470 (1)	2.39 (3)
N41	0.2331 (2)	0.7702 (2)	-0.2220 (1)	3.16 (4)
O41	0.1234 (2)	0.7516 (2)	-0.3427 (1)	4.21 (4)
O42	0.3512 (2)	0.9037 (1)	-0.1618 (1)	4.62 (5)
C5	0.1265 (2)	0.4590 (2)	-0.2209 (1)	2.55 (3)
C6	0.1166 (2)	0.3218 (2)	-0.1475 (1)	2.38 (3)
N61	0.0149 (2)	0.1494 (2)	-0.2244 (1)	3.11 (3)
O61	-0.0073 (2)	0.1267 (1)	-0.3458 (1)	4.17 (4)
O62	-0.0458 (2)	0.0367 (1)	-0.1638 (1)	4.50 (4)
N11	0.6408 (2)	-0.1932 (2)	0.5325 (1)	2.91 (3)
C12	0.5048 (2)	-0.0648 (2)	0.5502 (1)	2.64 (4)

respect to the phenyl-group plane by 11.25 (9), 15.4 (1) and 162.0 (1)°, respectively. The molecules are stacked in the *x* and *y* directions, stacking distances being 3.650 (3) and 3.744 (2) Å between molecules related by the site symmetries $-x$, $1-y$, $-z$ and $1-x$, $1-y$, $-z$, respectively.

The first interesting feature of this structure is that C—H⁺ donors of ethylenediamine and N—O⁻ acceptors of dinitrobenzoate are polarized to the extent that detectable C—H...O—N bonds operate towards stabilization of the structure in the lattice.

Though chelating, —COOH of dinitrobenzoic acid loses the proton to a neutral N atom of ethylenediamine which suggests a strong polarization of the

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

C1—C2	1.389 (2)	C1—C6	1.383 (1)
C2—C21	1.516 (1)	C2—C3	1.393 (2)
C21—O21	1.239 (2)	C21—O22	1.233 (2)
C3—C4	1.385 (1)	C4—C5	1.378 (2)
N41—O41	1.230 (1)	N41—O42	1.215 (2)
C5—C6	1.374 (2)	N61—O61	1.224 (2)
N61—O62	1.226 (2)	N11—C12	1.480 (2)
C12—C12'	1.509 (2)		
C2—C1—C6	118.6 (1)	C1—C2—C3	119.9 (1)
C1—C2—C21	120.3 (1)	C21—C2—C3	119.7 (1)
C2—C21—O22	116.2 (1)	C2—C21—O21	116.7 (1)
O21—C21—O22	127.1 (1)	C2—C3—C4	118.7 (1)
C3—C4—C5	123.0 (1)	C3—C4—N41	119.0 (1)
N41—C4—C5	118.1 (1)	C4—N41—O42	118.6 (1)
C4—N41—O41	117.2 (2)	O41—N41—O42	124.2 (1)
C4—C5—C6	116.5 (1)	C1—C6—C5	123.4 (1)
C5—C6—N61	117.3 (1)	C1—C6—N61	119.3 (1)
C6—N61—O62	118.2 (1)	C6—N61—O61	118.3 (1)
O61—N61—O62	123.5 (1)	N11—C12—C12'	112.6 (1)

N-atom lone pair by the proton of the carboxyl group and its ultimate transfer giving rise to 'self-complexation' (Poonia & Bajaj, 1979).

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Structure of Pentakis(dimethyl sulfoxide)dioxouranium(VI) Bis(tetrafluoroborate)

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Abstract. [(UO₂)(OSC₂H₆)₅][BF₄]₂, $M_r = 834.28$, triclinic, $P\bar{1}$, $a = 11.455$ (3), $b = 12.401$ (4), $c = 12.549$ (3) Å, $\alpha = 72.64$ (2), $\beta = 64.20$ (2), $\gamma =$

62.74 (2)°, $V = 1415$ (2) Å³, $Z = 4$, $D_x = 3.914$ g cm⁻³, $\text{Mo } K\alpha_1$, $\lambda = 0.71073$ Å, $\mu = 117.3$ cm⁻¹, $F(000) = 1600$, $T = 295$ K, $R = 0.035$ for