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1-{2-[4-(2,4-Dinitrophenyl)piperazin-1-yl]-ethyl}-4-aza-1-azoniabicyclo[2.2.2]octane chloride

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.046
wR factor = 0.085
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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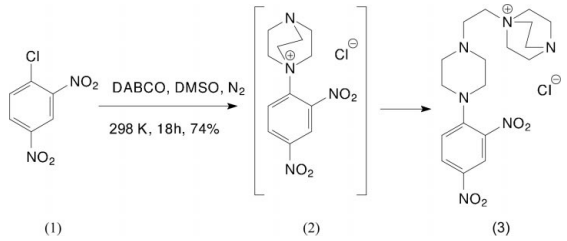
The title compound, $C_{18}H_{27}N_6O_4^+\cdot Cl^-$, is the product of addition of two molecules of DABCO (1,4-diazabicyclo[2.2.2]-octane) to one molecule of 1-chloro-2,4-dinitrobenzene. One of the DABCO molecules undergoes ring opening in the reaction, to give a piperazine ring, one N atom of which is connected to a 2,4-dinitrophenyl group, while the other is connected to an intact DABCO moiety *via* an ethylene linkage. The displaced chloride serves as counter-ion to balance the positive charge on the DABCO quaternary ammonium centre. The crystal structure determination confirms the structure deduced from NMR spectroscopy. Molecular dimensions are unexceptional.

Comment

It is well known that 1-chloro-2,4-dinitrobenzene (1) and 1-fluoro-2,4-dinitrobenzene undergo S_NAr displacement of the halogen with nitrogen and oxygen nucleophiles (March, 1992). In a synthetic project we attempted to displace chloride from (1) with the primary alcoholic function of a sensitive substrate under neutral conditions. However, this could not be achieved, so we sought to prepare a more electrophilic analogue of (1), in which the chloro substituent was replaced by a trialkylammonium function. This strategy has been successfully used to achieve displacements with alkoxide nucleophiles at the 6-position of 2-amino-6-(1-azonia-4-aza-bicyclo[2.2.2]oct-1-yl)purine chloride derived from reaction of 1,4-diazabicyclo[2.2.2]octane (DABCO) with 2-amino-6-chloropurine (Lembicz *et al.*, 1997). Other 'DABCO-purines' have been prepared and shown to react with nucleophiles (Lakshman *et al.*, 2000; Linn *et al.*, 1994). DABCO has also been used to catalyse reactions between 1-fluoro-2,4-dinitro-benzene and alcohols (Koeners *et al.*, 1980). However, the latter strategy was not useful for our purpose, as a mixture of products was obtained.



(1) (2) (3)

Based on the method of Lembicz *et al.* (1997), compound (1) was treated with an excess of DABCO in DMSO, with the intention of obtaining compound (2) by direct precipitation from the reaction mixture. After stirring overnight, the starting material had been consumed (TLC), but no precipitate had formed, so diethyl ether was added to induce preci-

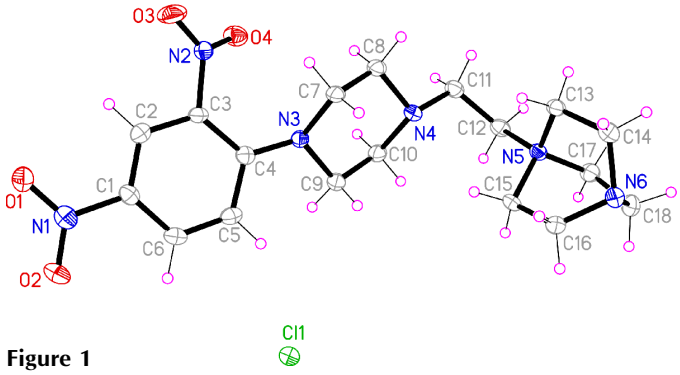


Figure 1
The molecular structure, with atom labels and 50% probability ellipsoids for non-H atoms.

pitation of the product, which was then recrystallized. The ^{1}H NMR spectrum of the resulting yellow solid showed more than the expected number of CH_2 groups, and elemental analysis indicated a 2:1 ratio of DABCO to 1-chloro-2,4-dinitrobenzene. This suggested structure (3), which was consistent with the ^{1}H NMR spectrum and was confirmed by the X-ray crystallographic study reported here. Compound (3) was previously reported (Ross *et al.*, 1963) as a product from reaction of (1) with DABCO in acetonitrile. Its structure was primarily validated at that time by a total synthesis. The formation of (3) was rationalized (Ross *et al.*, 1963) by postulating nucleophilic attack of chloride on intermediate (2), followed by displacement of chloride by DABCO, and also in a minor pathway, by direct attack of DABCO on intermediate (2). The reaction stops at (3) because chloride or DABCO attack on (2) is greatly facilitated by the 2,4-dinitrophenylpiperazino moiety of (3), acting as an excellent electron sink. Presumably, when DABCO reacts with 2-amino-6-chloropurine, 2-amino-6-(1-azonia-4-azabicyclo[2.2.2]oct-1-yl)purine chloride is obtained in high yield because it efficiently precipitates from the reaction mixture. A similar strategy was recently used to obtain a 9-substituted 2-amino-6-(1-azonia-4-azabicyclo[2.2.2]oct-1-yl)-purine (Lakshman *et al.*, 2000).

The molecular structure of (3) is shown in Fig. 1. The compound is a chloride salt of a quaternary ammonium cation. The cation contains a 2,4-dinitrophenyl group directly attached to one N atom of a piperazine ring, while the other N atom is linked by an ethylene tether to one N atom of a diazabicyclooctane (DABCO) group. All of these building blocks are very common in organic molecules, each occurring many times as structural fragments in entries in the Cambridge Structural Database (Version 5.25, November 2003; Allen, 2002). DABCO with a carbon substituent on one of its N atoms and no substituent on the other is found in only ten structures in the CSD, but the geometry of this relatively rigid group shows little variation, regardless of substitution. The piperazine ring has the expected chair conformation, with both substituents equatorial. The geometry of the 2,4-dinitrophenyl group is also unexceptional; the two nitro groups are twisted out of the benzene ring plane by 4.1 (3) and 33.0 (2)°, the larger twist being for the N2 nitro group, to reduce steric interaction with the adjacent piperazine ring.

The ethylene tether between N4 and N5 has a *gauche* conformation, with a torsion angle of −58.9 (3)° for N4—C11—C12—N5. This tether arises from N—C bond cleavage of a DABCO molecule during the reaction, resulting in two DABCO molecules being added to 1-chloro-2,4-dinitrobenzene, only one of which retains its bicyclic framework intact. There are no previously reported crystal structures containing this combination of an opened and an intact DABCO.

There are no unusual intermolecular interactions in the crystal structure, which contains no classical hydrogen bonds. Normal van der Waals and ionic interactions dictate the packing.

Experimental

1-Chloro-2,4-dinitrobenzene (1.20 g, 5.9 mmol) and DABCO (3.30 g, 29.3 mmol) in anhydrous DMSO (20 ml) were stirred under nitrogen at room temperature overnight. Diethyl ether (20 ml) was added and the resulting solution was stored at 277 K for 48 h. The precipitated yellow powder was collected by suction filtration and washed with diethyl ether and ethyl acetate. Recrystallization of the crude product from methanol-diethyl ether gave compound (3) as yellow crystals, 1.85 g (74%). A second, slow recrystallization from methanol–acetone, with a little diethyl ether to induce crystallization, yielded large yellow crystals suitable for X-ray diffraction.

Found: C, 50.45; H, 6.4; N, 20.1. Calc. for $C_{18}H_{27}ClN_6O_4$: C, 50.65; H, 6.35; N, 19.7%. NMR: δ_H (300 MHz, DMSO-d_6) 8.62 (*d*, J = 2.7 Hz, 1H, 3-H_{Ar}), 8.28 (*dd*, J = 2.7, 9.4 Hz, 1H, 6-H_{Ar}), 7.46 (*d*, J = 9.4 Hz, 1H, 5-H_{Ar}), 3.41 (*m*, 8H, 4 × CH_2N^+), 3.31 (*t*, J = 3.1 Hz, 4H, 2 × CH_2NAr), 3.03 (*t*, J = 7.2 Hz, 6H, 3 × DABCO CH_2N), 2.80 (*t*, J = 6.0 Hz, 2 H, $N^+CH_2CH_2N$), 2.50 (*s*, 4H, 2 × piperazine CH_2N); δ_C (75.45 MHz, DMSO-d_6) 149.1, 137.5, 137.3, 128.5, 123.9, 120.7, 59.7, 52.4, 52.2, 50.4, 50.3, 45.1.

Crystal data

$C_{18}H_{27}N_6O_4^+\cdot Cl^-$
M_r = 426.91
Monoclinic, $P2_1/n$
a = 6.9664 (14) Å
b = 24.389 (5) Å
c = 11.713 (2) Å
β = 97.63 (3)°
V = 1972.4 (7) Å^3
Z = 4
D_x = 1.438 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4679 reflections
θ = 2.9–27.5°
μ = 0.23 mm^{-1}
T = 150 (2) K
Block, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.93, T_{max} = 0.96
25990 measured reflections
3439 independent reflections
2443 reflections with $I > 2\sigma(I)$
R_{int} = 0.075
θ_{max} = 25.0°
$h = -8 \rightarrow 8$
$k = -29 \rightarrow 29$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.085
S = 1.04
3439 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 1.2199P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0028 (7)

H atoms were positioned geometrically and refined with a riding model, with C—H = 0.95–0.99 Å and with $U_{iso} = 1.2U_{eq}$(C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EvalCCD* (Duisenberg *et al.*, 2003); data reduction: *EvalCCD*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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