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Pentaerythritol trinitrate succinate: a hapten for pentaerythritol tetranitrate

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Key indicators

Single-crystal X-ray study
T = 306 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.043
wR factor = 0.132
Data-to-parameter ratio = 14.6

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

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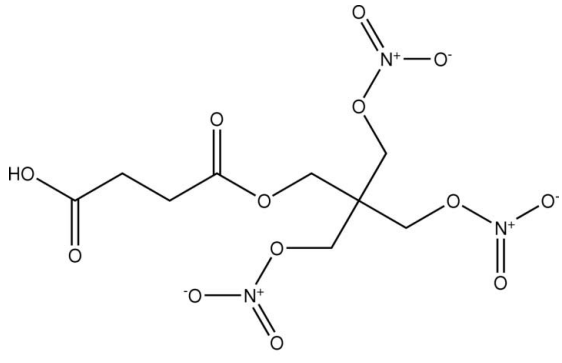
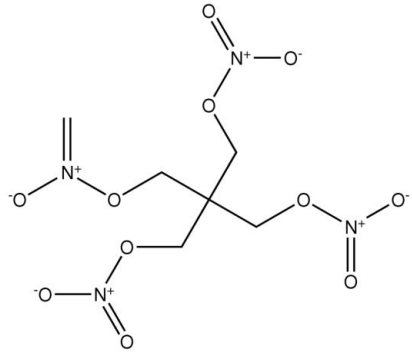
The title compound, $C_{10}H_{15}N_3O_{13}$, is a derivative of the energetic compound pentaerythritol tetranitrate (PETN). It is a hapten (a small molecule which can elicit an immune response only when coupled to a large carrier such as a protein) for PETN and was designed to be more stable and useful in immunochemistry.

Comment

The title compound, (I), is a hapten for PETN (Blackburn *et al.*, 2000). A hapten is a small molecule which can elicit an immune response only when coupled to a large carrier such as a protein. Coupling the hapten to a carrier prevents it from being cleared from the body.



(I)



PETN

The ongoing threat of terrorism using explosives [*e.g.* trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and pentaerythritol tetranitrate (PETN)], has focused research on new methods to detect these chemicals. Both RDX and PETN are commonly used high explosives that pose a serious risk to airport security. A major obstacle to their

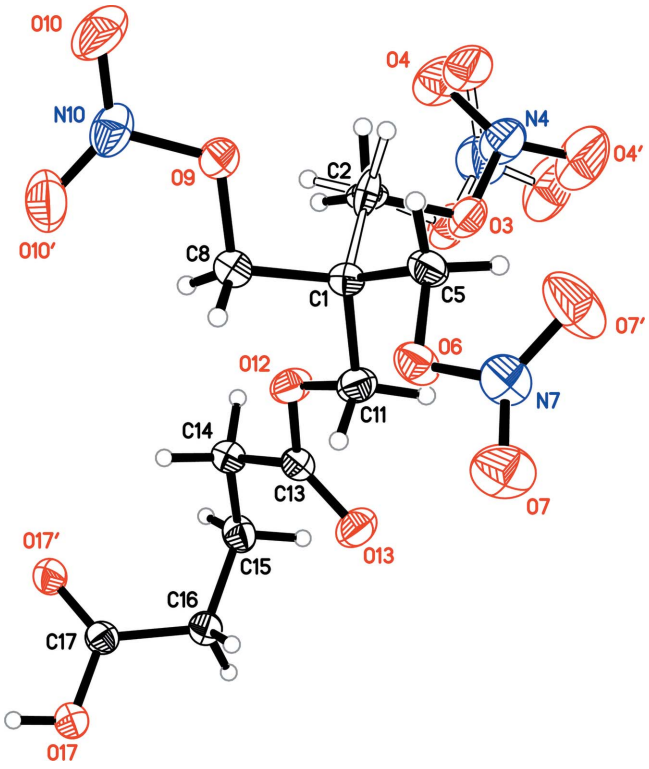


Figure 1
View of (I), showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at the 30% probability level. Both disorder components are shown.

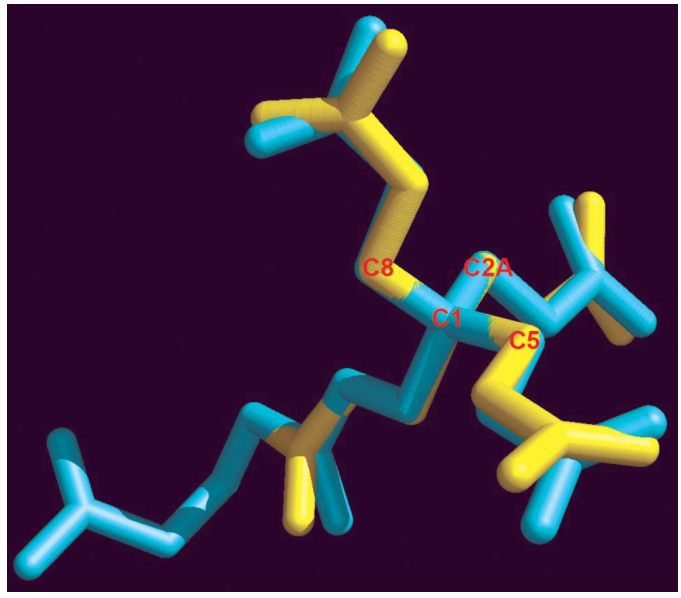


Figure 2
Comparison of (I) (blue) with PETN (yellow) (Trotter, 1963), showing the good agreement in the orientation of the nitro groups critical to recognition of the hapten by an antibody. The labeled atoms were used in producing the overlay. Only the major component of the disorder is shown.

detection is the presence of large amounts of plasticized filler material that can easily be molded and concealed. Because only small quantities are needed to produce significant damage, the ability to detect trace levels of these materials using highly sensitive and selective techniques could substantially reduce the security risks. Although physical methods (including X-rays and ion mobility spectroscopy) are the predominant technologies currently in use, immunochemical methods have also been developed for explosives detection (Goldman *et al.*, 2003; Charles *et al.*, 2004). These immunochemical methods rely on antibodies as the recognition element and derive their sensitivity and selectivity from the antibodies. In developing immunoassays for small molecules, the design and synthesis of an appropriate hapten and its coupling to a protein carrier (*i.e.* synthesis of a conjugate) are critical elements in defining assay sensitivity and selectivity.

The title compound, (I), crystallizes in the monoclinic space group $P2_1/n$ with a single molecule in the asymmetric unit. One of the three CH_2ONO_2 groups is disordered over two positions (Fig. 1).

For optimal results the hapten must be closely related to the target analyte in both its chemical structure and geometry. A comparison of (I) with PETN shows that the nitro groups of both molecules have similar geometries, confirming the choice of (I) as a hapten for PETN (Fig. 2).

Antibody recognition and immunoassay sensitivity are often determined by the distance between the surface and the tethered hapten. Thus, part of the design of the hapten–protein conjugate is the incorporation of a 'spacer'. In the case of (I), the spacer is the succinate substituent. The spacer allows for flexibility and a free range of motion of the binding groups, which can increase the interaction of the antibody and the hapten. In addition to providing flexibility, the spacer also serves to displace the hapten from a surface when the spacer is used to anchor the hapten to that surface. The surface could be a solid support used to immobilize the hapten for an assay or the surface of the carrier protein. The spacer in (I) separates the binding region from the surface by approximately 8.5 Å.

Experimental

The title compound was prepared as described previously (Blackburn *et al.*, 2000) and diffraction-quality crystals were grown by evaporation of a chloroform solution.

Crystal data

$C_{10}H_{15}N_3O_{13}$
M_r = 385.25
Monoclinic, $P2_1/n$
a = 10.3592 (9) Å
b = 11.9156 (10) Å
c = 13.4905 (11) Å
β = 92.637 (1)°
V = 1663.5 (2) Å^3
Z = 4
D_x = 1.537 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 306 (2) K
Plate, colorless
0.46 × 0.35 × 0.08 mm

Data collection

Bruker SMART APEX-II CCD diffractometer
ω scans
Absorption correction: multi-scan (*TWINABS*; Bruker, 2003)
T_{min} = 0.936, T_{max} = 0.989
7689 measured reflections
4028 independent reflections
2963 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 28.1°

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.25$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
4028 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
276 parameters	

The data crystal was twinned with one major component (mean I/σ = 11.2) and two minor components (mean I/σ = 5.6 and 5.0, respectively). The structure was solved using only non-overlapped reflections from the primary component. The structure was refined against both the non-overlapped data (7894 reflections) and the three-component twin data (51045 reflections). There was very little difference in the final refinement when comparing the non-overlapped data to the three-component twin. The refinement against the non-overlapped data is reported here. The disorder was modeled using the features of *SHELXTL* and the minor component restrained with the SAME instruction. The final occupancy ratio of the two components of the disorder was 0.67:0.33.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005) and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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