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Tuning the synthesis of a dinitroaromatic towards a new trinitroaromatic stabilized energetic material

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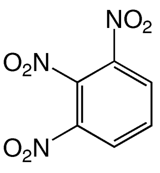
A new isomer of diaminotrinitrobenzene, **3**, has been prepared from 1,2-diaminobenzene under high dilution conditions in which the two NH_2 electron-donating groups increase the thermal stability of the 1,2,3-trinitrobenzene backbone. Its thermal decomposition only begins around 230 °C and deflagration occurs at 298 °C, which is of interest for heat-resistant explosives. The crystal structure of the known 1,2-diamino-4,5-dinitrobenzene, **4**, which has been obtained in place of **3** under different dilution conditions, is also reported and reveals interesting van der Waals and intermolecular N–H···O–N hydrogen-bonding interactions.

Introduction

Energetic materials are metastable molecules endowed with high reactivity and numerous studies have been performed to develop capabilities to predict the sensitivity of explosives,[1] that is, the ease with which these molecules undergo explosive decomposition by application of stimuli, producing smaller molecules and large amounts of energy.[2] Aromatic compounds with nitro groups are known to be potential explosives,[3] particularly when the number of nitro groups per ring is equal or superior to 3. In general, the power of an explosive molecule and its sensitivity increase with the number of NO_2 groups.[4] Explosives with high-temperature properties, usually called "heat-resistant explosives", or secondary explosives, are the subject of intensive research and the relationship between their high thermal stability and their molecular and crystal structures are not yet fully understood.[3] Previous works reported that the best way to generate much safer nitroaromatics, as for example, to desensitize a trinitro explosive while still keeping its explosive power, is to increase the number of electron-donating groups (*e.g.*, NH_2).[2] This has allowed the reduction of trinitrotoluene (TNT)[5] sensitivity by factors of 3 or 4.[2] Furthermore, the amino substituents in TNT bring about an added benefit since the hydrogen bonding interactions between NO_2 and NH_2 groups increase the bulk density and thus the power, while providing desensitization.[2] Trinitroaromatic molecules bearing an amino group represent a class of energetic materials classified as secondary explosives.[3] For example, 1,2,3-trinitrobenzene, **1**,[6,7] is the parent molecule to secondary explosives such as **2**, [6–8] which is stabilized due to the presence of an amino group.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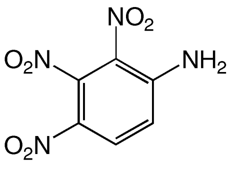
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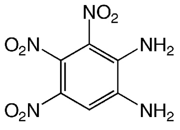
Therefore, we anticipated that further addition of an electron-donating substituent (*e.g.*, $-NH_2$) could give access to an even more stabilized form of 1,2,3-trinitrobenzene. Polynitroaromatic molecules can be prepared by direct oxidation of amines, which represents a convenient methodology owing to the availability of amines and the resulting high yields of the reactions.[7,9] Polynitroaromatics bearing amino groups may be synthesized by nucleophilic aromatic substitution[10,11] or by direct amination of nitrobenzene derivatives, proceeding by vicarious nucleophilic substitution of hydrogen.[12,13] However, some polynitroaromatic compounds are still not accessible. This was the case until now for the new isomer 1,2-diamino-3,4,5-trinitrobenzene **3**, for which we report a three-step synthesis from 1,2-diaminobenzene under high dilution conditions (Scheme 1). Under different dilution conditions,[14] 1,2-diamino-4,5-dinitrobenzene, **4**, is isolated instead. Since this molecule has previously given rise to numerous theoretical calculations of its hyperpolarizability and electronic properties in relation to nonlinear optical properties,[15–17] we decided to determine its precise structure by X-ray diffraction analysis.

To the best of our knowledge, only one isomer of **3** appears to have been reported so far, 1,3-diamino-2,4,6-trinitrobenzene, **5**, in which the nitro groups are not in sequential positions.[18] Depending on the nature of the stimulus that triggers explosive decomposition, different types of sensitivity can be defined, such as heat, impact or shock, but also friction and electrostatic sensitivity.[2] In the present study, only thermal behaviour will be discussed.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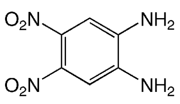
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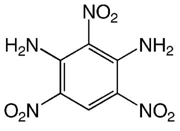
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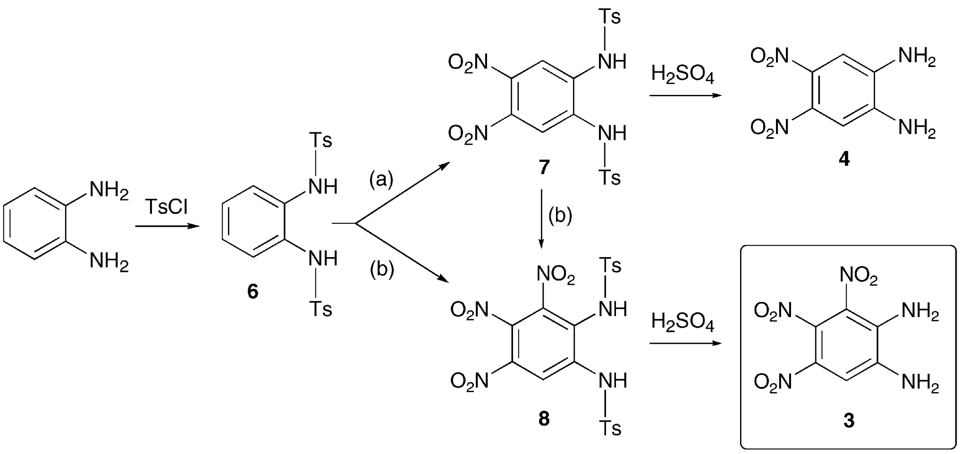
Results and discussion

Nitration of 1,2-diaminobenzene itself is not feasible and *N*,*N*′-protected derivatives have been generally used for the preparation of nitro compounds bearing two amino groups.[14] In the course of the preparation of 1,2-diamino-4,5-dinitrobenzene, **4**, an intermediate in the synthesis of functional ligands, we observed that, following the described procedure (route a, Scheme 1),[14] intermediate **7** remained partly soluble although it was reported to precipitate in AcOH. Therefore, we anticipated that if the same reaction was carried out under high



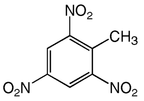
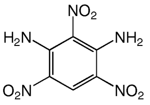
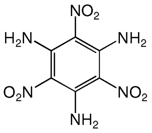
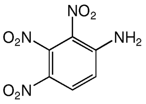
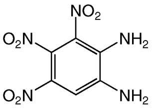
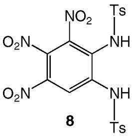
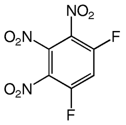
Scheme 1 Synthesis of **3**. (a) HNO_3/glacial AcOH, low dilution conditions; (b) HNO_3/glacial AcOH, high dilution conditions.

dilution conditions, precipitation of **7** could be prevented and further nitration facilitated. Whereas treatment of **6** with concentrated fuming HNO_3/glacial AcOH under low dilution conditions afforded **7** in high yield, we have now found that the same reaction carried out under high dilution conditions leads instead to **8**, which can be subsequently deprotected into **3** (route b, Scheme 1).

Compound **8** was fully characterized except by X-ray diffraction and its ^1H NMR data were consistent with the presence of three nitro groups that lower the molecular symmetry present in **7**. Thus, the methyl groups of the tosyl moieties in **8** give rise to two singlets at δ 2.45 and 2.48, in contrast to **7** for which the tosyl groups appear as a singlet at δ 2.41. Detosylation was carried out in concentrated H_2SO_4 at 90 °C and recrystallization from a mixture of acetone–H_2O afforded **3** as orange crystals. **3** revealed, as expected, a high thermal stability since the product begins to decompose , with a disappearance of the orange colour, only around 230 °C (gradient of 5 °C min^{-1}). The measurements were made with specific safety precautions on a *ca.* 0.5 mg sample. For comparison, thermal data of related molecules are reported in Table 1. These data show the very significant thermal stabilization brought by the introduction of electron-donating groups on the trinitrobenzene skeleton.[19] In the case of substituted 1,3,5-trinitrobenzene derivatives, the thermal stability of the material increases with the number of NH_2 groups as indicated by the values of the melting (or decomposition) point of TNT, **5** and **9**, the former being among the most stable trinitrobenzene derivatives[20] (Table 1). Similarly, when 1,2,3-trinitrobenzene, **1**,[7] is stabilized by the presence of one NH_2 group, as in molecule **2**,[7] the melting (or decomposition) temperature increases from 121–122 to 208–210 °C. Introduction of a second amino substituent, as in **3**, leads to an even higher stability, with a decomposition temperature of 230 °C. Compared to **3**, *N*-substitution by electron-withdrawing groups such as tosyls in **8** destabilizes the trinitroaromatic molecule (m.p. = 185 °C). Consistently, introduction of fluorine atoms in **10** destabilizes the parent molecule **1** (m.p. = 88–90 *vs.* 121–122 °C).[7] Note however, that TNT is less stable than 1,3,5-trinitrobenzene, even though the methyl group is more electron-donating than hydrogen.[21]

Compound **3** was found to decompose with deflagration at 298 °C. Recrystallization from MeCN instead of a mixture of acetone–H_2O afforded **3** as brown crystals, which decomposed with deflagration at 290 °C. The temperature at which this sample begins to decompose could not be determined with precision due to its darker colour, itself suggesting a different packing arrangement in the solid state relative to that in the orange crystals.[22]

Table 1 Thermal stability data for trinitroaromatic molecules

Compound	M.p./°C	Reference
 **TNT**	82	23
 **5**	225–228	24
 **9**	>365	20
 **1**	121–122	7
 **2**	208–210	7
 **3**	230[a]	This work
 **8**	185	This work
 **10**	88–90	7

[a] Here, it is clearly a decomposition rather than a melting point.

Table 2 Crystallographic data for **4**

Chemical formula	$C_6H_6N_4O_4$
Formula weight/g mol^{-1}	198.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.7780(10)
b/Å	5.6200(10)
c/Å	15.635(2)
β/°	98.504(5)
U/Å^3	762.83(19)
Z	4
ρ_{calcd}/g cm^{-3}	1.725
μ(MoKα)/mm^{-1}	0.147
Temperature/K	173(2)
Total reflections	5056
Unique reflections	2215
R_{int}	0.0421
Observed data [$I > 2\sigma(I)$]	1670
R_1	0.0489
wR_2	0.1124

Although **4** is a long-known compound[14] that has given rise to numerous theoretical calculations regarding NLO properties (investigations on the electrostatic first hyperpolarizabilities of different chromophores with various donor-acceptor pairs),[15–17] no X-ray structure has been reported so far despite its potential to reveal interesting repulsive intramolecular and attractive intermolecular interactions, depending on the degree of internal rotation of the amino and nitro groups about the C–N bonds.[25] Single crystals of **4**, suitable for an X-ray diffraction study, were grown from acetone. Crystallographic data and selected bond lengths and angles are given in Tables 2 and 3, respectively.

Compound **4** crystallizes in a centrosymmetric space group, which rules out second-order NLO properties in the solid state. Its crystal structure determination revealed that the nitrogen atoms N(3) and N(4) are not coplanar with the aromatic ring, in contrast with the amino nitrogen atoms N(1) and N(2). This results from the steric hindrance between the NO_2 groups, which are twisted with respect to the phenyl ring (Fig. 1), as already observed in other *o*-dinitrobenzene derivatives.[26]

Examination of the bond distances (Table 3) shows that the two C–NH_2 bonds [1.360(2) and 1.372(2) Å] are shorter than the C–NO_2 bonds [1.451(2) Å], which is consistent with previous structural data collected on aromatic compounds bearing amino and nitro groups.[27] In the solid state, van der Waals interactions lead to the formation of parallel sheets as indicated by the separations between atoms facing each other in two successive layers, with C(3B)···N(3E), C(6A)···C(6D) and N(1A)···N(4D) distances of 3.551(5), 3.218(5) and 3.411(5) Å, respectively (Fig. 2). Within each of these layers, all the chromophores are arranged in alternating orientations along the C(3D)–C(6D) molecular axis and assembled *via* N–H···O–N hydrogen bridges of 2.439(4) and 2.554(4) Å (Table 4).

Fig. 3 illustrates the intermolecular packing in which a central layer can be identified where each molecule interacts with four neighbours from the adjacent layers *via* N–H···O–N hydrogen bonds in the range 2.428(4)–2.552(4) Å (Table 4). Inter- and intralayer hydrogen bonding distances are similar and reveal a highly bifurcated system that forms a three-dimensional network.

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

C(1)–N(1)	1.360(2)	C(5)–C(6)–C(1)	121.5(1)
C(2)–N(2)	1.372(2)	C(4)–C(3)–C(2)	121.7(1)
C(4)–N(3)	1.451(2)	C(6)–C(1)–0(1)	120.2(1)
C(5)–N(4)	1.451(2)	C(3)–C(2)–N(2)	121.0(1)
C(1)–C(2)	1.423(2)	C(3)–C(4)–N(3)	117.5(1)
C(4)–C(5)	1.396(2)	C(6)–C(4)–N(4)	116.9(1)
O(1)–N(3)	1.231(2)	C(5)–C(4)–N(3)	122.9(1)
O(2)–N(3)	1.230(2)	C(1)–C(2)–N(2)	120.2(1)
O(3)–N(4)	1.230(2)	C(6)–C(5)–C(4)	119.9(1)
O(4)–N(4)	1.226(2)	C(4)–C(5)–N(4)	122.7(1)

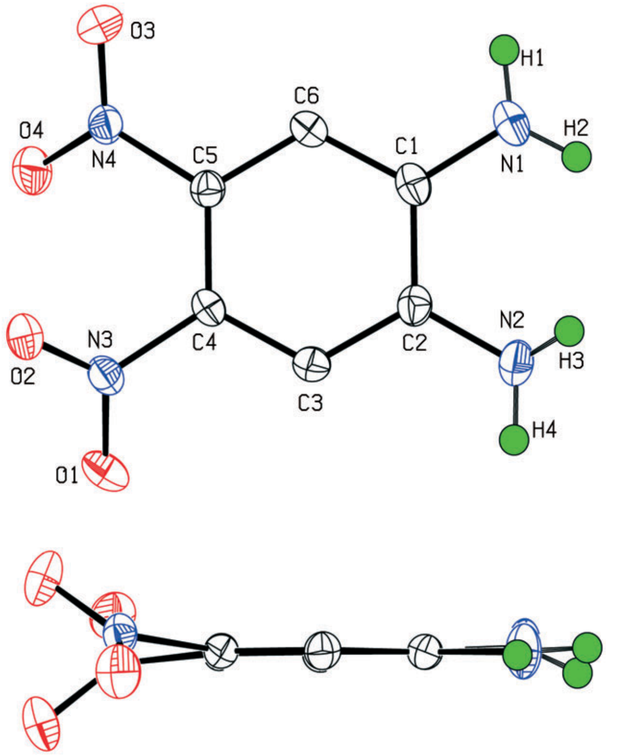


Fig. 1 ORTEP representations of the molecular structure of **4** in the crystal.

Conclusion

3 constitutes the second known isomer of diaminotrinitrobenzene and reveals a high thermal stability for an explosive

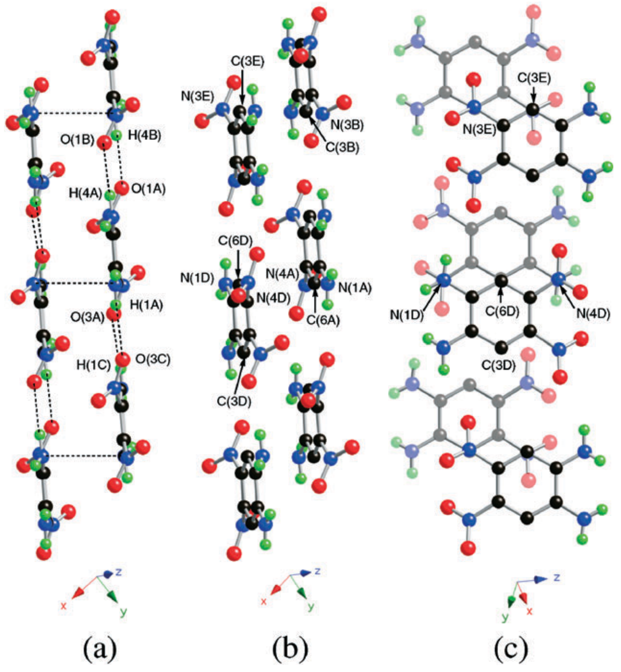


Fig. 2 (a) Side view of the stacking arrangement generated by **4** in the solid state. (b) Intermediate view. (c) View of the sheet structure generated by **4** in the solid state. Colour coding: nitrogen, blue; oxygen, red; hydrogen, green. For clarity, the neighbouring molecules have been labelled A–E.

Table 4 Selected non-covalent interaction distances (Å) in **4**

	Symmetry transformations used to generate equivalent atoms
Intramolecular interactions (Fig. 1)	
H(2)···N(2) = 2.525(4)	
H(3)···N(1) = 2.555(4)	
Intermolecular interactions (Fig. 2)	
O(1A)···H(4B) = 2.439(4); O(1A)···N(2B) = 3.286(5)	$-x, 2 - y, -z$
O(3A)···H(1C) = 2.554(4); O(3A)···N(1C) = 3.358(5)	$1 - x, -y, -z$
C(6A)···C(6D) = 3.218(5)	$1 - x, 1 - y, -z$
N(1A)···N(4D) = 3.411(5)	$1 - x, 1 - y, -z$
C(3B)···N(3E) = 3.551(5)	$-x, 2 - y, -z; x, 1 + y, z$
Intermolecular interactions (Fig. 3)	
H(2A)···O(2F) = 2.552(4); N(1A)···O(2F) = 3.319(5)	$1/2 + x, 3/2 - y, 1/2 + z$
H(3A)···O(2F) = 2.434(4); N(2A)···O(2F) = 3.231(5)	$1/2 + x, 3/2 - y, 1/2 + z$
O(4A)···H(2G) = 2.428(4); O(4A)···N(1G) = 2.916(5)	$-1/2 + x, 1/2 - y, -1/2 + z$
H(2A)···O(4H) = 2.428(4); N(1A)···O(4H) = 2.916(5)	$1/2 + x, 1/2 - y, 1/2 + z$
O(2A)···H(2I) = 2.552(4); O(2A)···N(1I) = 3.319(5)	$-1/2 + x, 3/2 - y, -1/2 + z$
O(2A)···H(3I) = 2.434(4); O(2A)···N(2I) = 3.231(5)	$-1/2 + x, 3/2 - y, -1/2 + z$

compound. Its synthesis represents a simple and new approach in the preparation of trinitrobenzene derivatives, which proceeds by a nitration reaction under high dilution conditions. Furthermore, such molecules often display unique chemical and electrochemical properties that should attract the interest of chemists.[28] The determination of the crystal structure of **4** by X-ray diffraction provides new structural data on packing arrangements in aminonitro aromatic compounds resulting from van der Waals interactions and N–H···O–N hydrogen bonds. Such data will also be useful for a better understanding of the factors governing the conformation of the nitro groups in polynitroaromatic compounds bearing amino substituents since molecular structures have been recently established mostly by theoretical calculations.[1,8,15–17] It is noteworthy that experimental studies on the polymorphism of 1,3,5-trinitrobenzene[29] and on the crystal structures of reduction products of TNT have appeared very recently.[30]

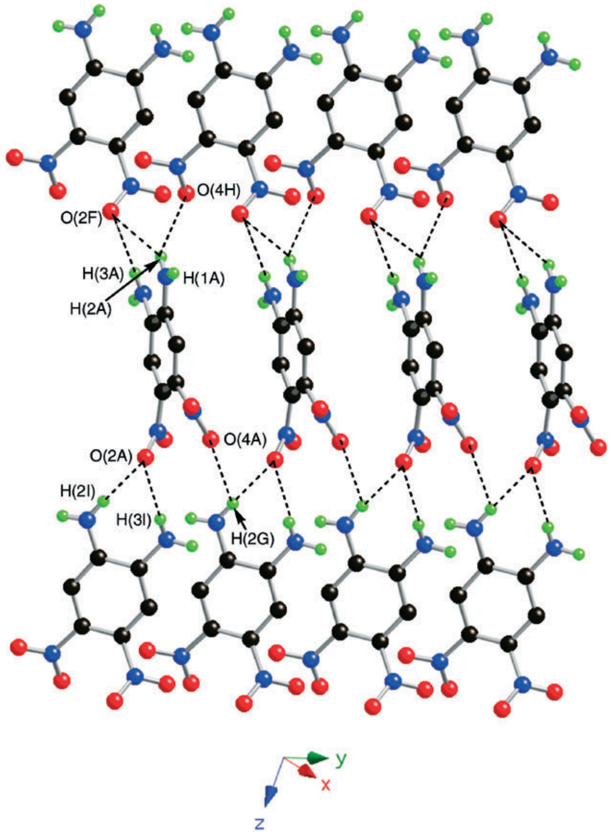


Fig. 3 View of the N–H···O–N hydrogen-bonding network in the solid state structure of **4**. Colour coding: nitrogen, blue; oxygen, red; hydrogen, green.

Experimental

General

^{1}H NMR (300 MHz) spectra were recorded on a Bruker AC-300 instrument. FAB mass spectral analyses were recorded on an Autospec HF mass spectrometer and EI mass spectral analyses were recorded on a Finnigan TSQ 700. Elemental analyses were performed by the Service de Microanalyse, Université Louis Pasteur, Strasbourg. Compounds **4**, **6** and **7** were prepared as reported in the literature.[14]

Syntheses

Compound 8. To a solution of **6** (1.00 g, 2.40 mmol) in a large volume of glacial AcOH (1 L) was added at room temperature a large excess of a mixture of fuming nitric acid and glacial acetic acid (4 : 5 v/v). The mixture was stirred for 7 h at 60 °C and 12 h at room temperature. The solution was then evaporated to dryness under reduced pressure and the residue was taken up in EtOH. The suspended solid was collected by filtration and dried to afford **8** as a white powder (0.86 g, 65% yield). ^{1}H NMR (300 MHz, d$_6$-acetone), δ = 2.45 (s, 3H, CH$_3$), 2.48 (s, 3H, CH$_3$), 7.44 (m, 4H, H$_{\text{arom}}$), 7.67 (d, 2H, H$_{\text{arom}}$), 7.89 (d, 2H, H$_{\text{arom}}$), 8.48 (s, 1H, H$_{\text{arom}}$). The two N–H resonances could not be observed at room temperature. MS (FAB): m/z = 552.0 [M + 1]$^+$. Anal. calcd for $C_{20}H_{17}N_5O_{10}S_2$: C, 43.56; H, 3.11; N, 12.70; found: C, 42.93; H, 3.12; N, 12.02. M.p. (decomp.) = 185 °C.

Compound 3. A solution of **8** (0.86 g, 1.56 mmol) in concentrated sulfuric acid was stirred at 90 °C for 4 h. The mixture was then cooled to room temperature and poured into water. Solid Na_2CO_3 was added slowly until basic pH was reached, then the solution was left for 12 h without stirring. An orange precipitate formed and was collected by filtration and washed with water to afford **3**, which was further purified by recrystallization from a mixture of acetone–H_2O (0.15 g, 40% yield). Note that problems were observed in reproducing the crystallization step. ^{1}H NMR (300 MHz, d$_6$-acetone), δ = 6.10 (br s, 1.7 H, NH$_2$), 7.05 (br s, 1.7 H, NH$_2$), 7.48 (s, 1 H, H$_{\text{arom}}$). The NH$_2$ proton integration does not account for exactly 2H each, due to proton exchange occurring with water present in the solvent (a similar observation was made with **4** in d$_6$-acetone). The addition of a drop of D_2O led to immediate disappearance of the NH$_2$ signals. MS (EI, 40 eV): m/z = 243 [M]$^+$. Anal. calcd for $C_6H_5N_5O_6$: C, 29.64; H, 2.07; N, 28.80; found: C, 29.95; H, 2.44; N, 28.73. M.p. (decomp.) = 230 °C.

X-Ray analysis

A single crystal of **4** suitable for X-ray analysis (obtained by slow evaporation of an acetone–H_2O mixture) was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, λ = 0.710 69 Å). A list of data collection conditions (Denzo software) and structure refinements are given in Table 2. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, which were not found by Fourier differences, were generated according to stereochemistry and refined using a riding model in SHELXL97.[31]†

Acknowledgements

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22 A major exothermic peak was observed by TGA at 274 °C (G. Jacob, personal communication). This may be due to differences in the molecular packing and/or crystallinity of the various samples. The onset temperature of **3** was measured at 251 °C, which is lower than that of its positional isomer **5** (*ca.* 295 °C[2]).
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