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Base-Induced Cycloaddition of Tosylmethyl or (*tert*-Butoxycarbonyl)methyl Isocyanide to 1,4-Disubstituted 2,3-Dinitro-1,3-butadienes. Access to 2,3-Disubstituted 4-Ethynylpyrroles[1]

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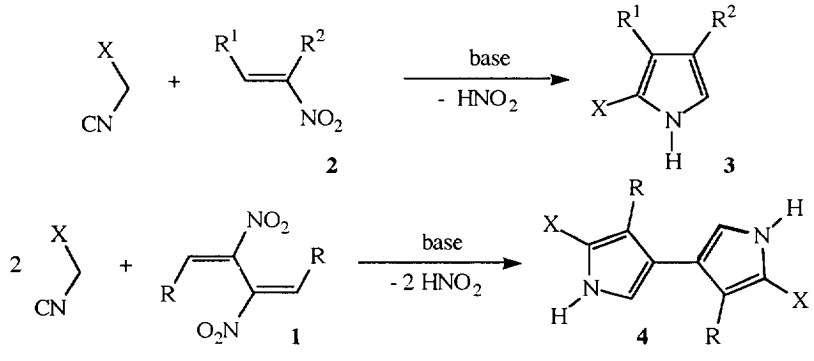
Abstract : The reactions of 1,4-disubstituted 2,3-dinitro-1,3-butadienes **1a-g** in THF with isocyanides XCH_2NC (TosMIC, X = tosyl; TBICA, X = $COOBu^t$) and DBU furnish good to moderate yields of 2,3-disubstituted 4-ethynylpyrroles **5a-g** or **6a-g**. In the reaction of **1g** with TosMIC and DBU the nitrovinyl pyrrole **7g** and the 3,3'-dipyrrole **4g** are also isolated as by-products. A mechanism involving sequential base-induced addition, elimination and cyclization steps is advanced to account for the formation of the isolated products.

The base-induced reactions of substituted methylisocyanides with both alkene[2] and 1,3-butadiene[3] Michael acceptors represent an interesting access to pyrroles and, consequently, to their important chemistry.[4] In connection with our studies[5] on the synthetic exploitation of the ring-opening of 3,4-dinitrothiophene and in particular on the chemical behaviour of the therefrom easily accessible 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes **1**, special relevance is attached to the reactions[2a-c] of 1-nitroalkenes **2** with methylisocyanides which lead to pyrroles of type **3** via a base-induced addition-cyclization-elimination process.[2a] On these grounds (Scheme 1) we conceived that the application of the mentioned reactions to dinitrobutadienes **1** would lead[3b,d] to interesting target molecules such as substituted 3,3'-dipyrroles **4**.

Scheme 1



In this work we report on the results obtained from the study of the base-induced reactivity of dinitrobutadienes **1** with two representative isocyanides as tosylmethylisocyanide (TosMIC) and *tert*-butyl isocyanoacetate (TBICA). Such results show that the behaviour of the dinitrobutadiene system of **1** like two independent 1-nitroalkene functionalities (as forecasted in Scheme 1) is once again[5b] not warranted at all: a novel reaction takes place leading to substituted ethynylpyrroles, otherwise not easily accessible compounds.

RESULTS AND DISCUSSION

Preliminary screening of the reaction of 1,4-bis(4-methylphenyl)-2,3-dinitro-1,3-butadiene ***1a*** *with TosMIC and X-ray crystallographic analysis of the obtained product.*

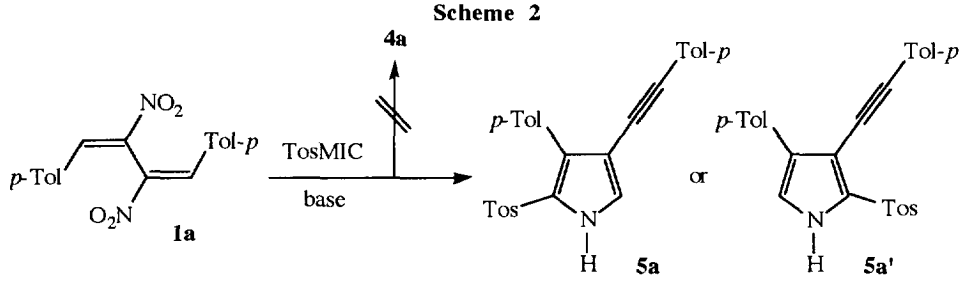
In order to investigate on the possible formation of the 3,3'-dipyrrole derivative (**4a**, R = 4-methylphenyl, X = tosyl), the reactions of dinitrobutadiene **1a** were carried out with two molar equivalents of TosMIC in various base/solvent systems (Table 1, expts 1-6). Contrary to expectations, in such preliminary investigation not even a trace amount of 3,3'-dipyrrole **4a** could be detected in the final reaction mixtures. Actually, as shown in Scheme 2, the reactions of **1a** with TosMIC gave variable yields of a product ($C_{27}H_{23}NO_2S$) to which, on the grounds of microanalytical data and of ^1H and ^{13}C NMR spectra, the structure of either 3-(4-methylphenyl)-4-[(4-methylphenyl)ethynyl]- (**5a**) or 4-(4-methylphenyl)-3-[(4-methylphenyl)-ethynyl]-2-[(4-methylphenyl)-sulfonyl]pyrrole (**5a'**) could be tentatively assigned. On the basis of such structures, the formation of the isolated product from **1a** has to be bound up with an addition-cyclization of a single TosMIC molecule, with the overall elimination of two nitrous acid molecules and with the consumption of two base equivalents as required

Table 1. Reactions of dinitrobutadiene **1a** with TosMIC[a] in various base-solvent systems[b]

Expt	Solvent	Base	Time (h)[c]	Product yield (%)[d]
1	MeCN	DBU[e]	0.5	52
2	DMF	DBU	1.0	65
3	DMSO	DBU	0.5	56
4	THF	TMG[f]	0.5	37
5	THF-Pr^{i}OH[g]	DBU	0.5	58
6	THF	DBU	0.5	67
7	THF[h]	DBU	0.5	76

a) Tosylmethylisocyanide. b) [**1a**] = 0.25 M, [TosMIC] = [base] = 0.5 M, unless otherwise specified. c) Reaction times determined following by TLC the disappearance of **1a**. d) Yields of product ($C_{27}H_{23}NO_2S$) isolated by chromatography. e) 1,8-Diazabicyclo-[5.4.0]undec-7-ene. f) 1,1,3,3-Tetramethylguanidine. g) 1:1 Mixture (v/v) as in analogous reactions on 1-nitroalkenes (ref. 2a). h) [**1a**] = 0.25 M, [TosMIC] = 0.27 M, [DBU] = 0.5 M.

Scheme 2



by equation 1. Accordingly, in expts 1-6 of Table 1 consistent amounts of unreacted TosMIC were recovered (0.8-0.9 moles out of the two employed) and expt 7 carried out with stoichiometric amounts of reagents gave the best yield of product.

1a + TosMIC + 2 B ⟶ **5a** (or **5a'**) + 2 $BH^+NO_2^-$ (equation 1)

The definitive assignment of the structure **5a** to the reaction product could be achieved through its X-ray crystallographic analysis. The molecular structure of **5a** is shown in Figure 1; selected bond distances and bond angles are reported in Table 2. Geometric parameters for **5a** are in the normal range; in particular, bond distances are in good agreement with average values[6] taken from the Cambridge Structural Database,[7] and the geometry of the ethynyl group fairly agrees with that reported for the one known structure of a 3-ethynylpyrrole derivative, 5-[*N,N*-bis(trimethylsilyl)amino]-2-cyano-4-trimethylsilyl-3-[(trimethylsilyl)ethynyl]pyrrole.[8]

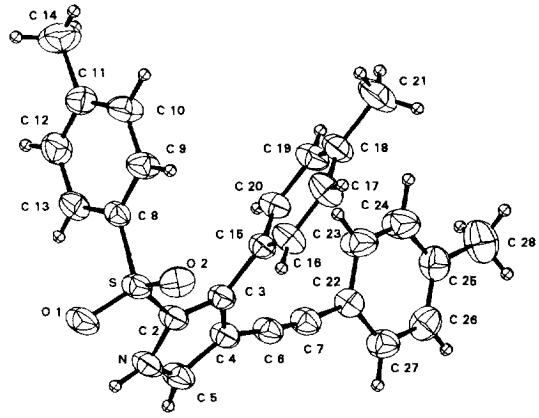


Figure 1. ORTEP view of the structure of **5a** with numbering of atoms. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms, treated as isotropic, are on an arbitrary scale.

Table 2. Selected bond lenghts (Å) and angles(°) for **5a**.

S-O(2)	1.434(2)	C(11)-C(14)	1.514(4)	C(2)-C(3)-C(4)	106.0(2)
S-O(1)	1.439(2)	C(18)-C(21)	1.513(3)	C(2)-C(3)-C(15)	128.4(2)
S-C(2)	1.744(2)	C(25)-C(28)	1.515(4)	C(4)-C(3)-C(15)	125.5(2)
S-C(8)	1.759(2)	O(2)-S-O(1)	118.32(12)	C(5)-C(4)-C(3)	107.1(2)
N-C(5)	1.337(3)	O(2)-S-C(2)	111.08(12)	C(5)-C(4)-C(6)	127.6(2)
N-C(2)	1.369(3)	O(1)-S-C(2)	105.36(11)	C(3)-C(4)-C(6)	125.2(2)
C(2)-C(3)	1.377(3)	O(2)-S-C(8)	108.02(11)	N-C(5)-C(4)	108.9(2)
C(3)-C(4)	1.422(3)	O(1)-S-C(8)	108.60(11)	C(7)-C(6)-C(4)	173.9(2)
C(3)-C(15)	1.474(3)	C(2)-S-C(8)	104.60(11)	C(6)-C(7)-C(22)	173.5(2)
C(4)-C(5)	1.378(3)	C(5)-N-C(2)	109.3(2)	C(9)-C(8)-S	120.0(2)
C(4)-C(6)	1.427(3)	N-C(2)-C(3)	108.6(2)	C(13)-C(8)-S	120.3(2)
C(6)-C(7)	1.193(3)	N-C(2)-S	119.3(2)	C(23)-C(22)-C(7)	119.4(2)
C(7)-C(22)	1.429(3)	C(3)-C(2)-S	131.3(2)	C(27)-C(22)-C(7)	122.6(2)

Hydrogen bond:	Donor-H	Donor···Acceptor	H···Acceptor	Donor-H···Acceptor
	N-H1	N···O1 *	H1···O1 *	N-H1···O1
	0.92(.03)	2.899(.003)	2.03(.03)	156.8(2.5)

* Equivalent position: 2-x, 2-y, -z

Table 3. Least-squares planes in **5a**. Standard deviation in parenthesis.

Plane	Atoms defining the plane	Highest deviation (Å)	Dihedral angles (°)
A	N, C(2) to C(5)	0.006(2)	
B	C(8) to C(13)	0.016(3)	B-A 86.4(1)
C	C(15) to C(20)	0.010(3)	C-B 41.7(1)
			C-A 47.9(1)
D	C(22) to C(27)	0.002(3)	D-C 69.9(1)
			D-B 89.9(1)
			D-A 39.3(1)

The deviations of plane-defining atoms from least-squares planes and the dihedral angles between the latter ones are summarized in Table 3. In the crystal a hydrogen bond N-H(1)···O(1) connects molecules in couples through a centre of symmetry (see Table 2). Apart from few rather close intermolecular distances (C14···C14 in 1-x, 1-y, 1-z, 3.716 Å; C12···C28 in 1+x, -1+y, z, 3.502 Å) there are no short contacts in the structure.

Reactions of dinitrobutadienes ***1a-h*** *with TosMIC or TBICA.*

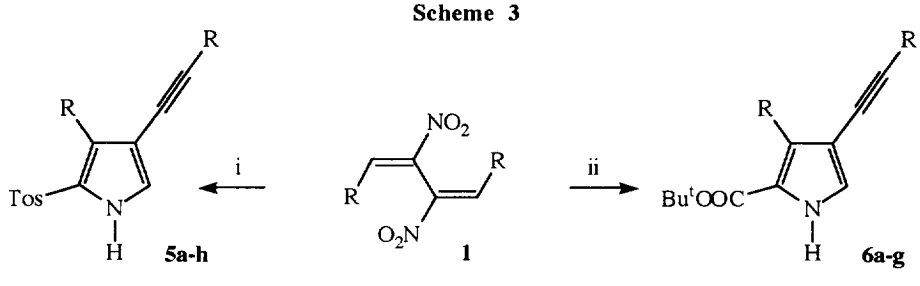
In order to test the generality of the process leading to substituted 4-ethynylpyrroles, the optimized conditions found for the base-induced reaction of the model substrate **1a** with TosMIC (expt 7, Table 1) were extended to 1,4-disubstituted 2,3-dinitro-1,3-butadienes **1b-h**. Under similar conditions, moreover, the reactivity of dinitrobutadienes **1a-g** with *tert*-butyl isocyanoacetate (TBICA) was also investigated.

The obtained results (Scheme 3, Table 4) show that the treatment of 1,4-dialkyl- and 1,4-diaryl-2,3-dinitro-1,3-butadienes with one molar equivalent of either TosMIC or TBICA and two molar equivalents of DBU in THF always results in the formation of the corresponding 2-tosyl or 2-*tert*-butoxycarbonyl 4-ethynylpyrrole derivatives **5a-h** or **6a-g**, respectively.

The data reported in Table 4 reveal that, while for the reactions carried out on the benzene derivatives **1a-d** the yields of both **5a-d** and **6a-d** are satisfactory, such yields drop to low values for the 1-naphthyl **1e** and for the 2-thienyl derivative **1f**. With the latter substrates, moreover, using TBICA as reagent the yields of **6e** and **6f** are roughly halved with respect to those of the corresponding pyrroles **5e** and **5f.**

It must be stressed, on this regard, that in all the reactions investigated the formation of pyrroles **5** and **6** is always accompanied by tars. Most likely the latter arise from a base-induced polymerization of dinitrobutadienes as, consistently, a substantial decomposition (whose rate depends on the nature of the substrate) was independently ascertained to occur when such nitroderivatives were allowed to react with DBU under otherwise

Scheme 3



i) THF/TosMIC (1.1 mol. equiv.)/DBU (2 mol. equiv.); ii) THF/TBICA (1.1 mol. equiv.)/DBU (2 mol. equiv.)

Table 4. Reactions of dinitrobutadienes **1a-h** with either TosMIC[a] or TBICA[b] and DBU in THF[c]

Expt	Substr.	R=	Isonitrile	Product	Yield (%)[d]
1	**1a**	4-MeC_6H_4	TosMIC	**5a**	76
2	**1b**	2-MeC_6H_4		**5b**	82
3	**1c**	4-$MeOC_6H_4$		**5c**	71
4	**1d**	phenyl		**5d**	72
5	**1e**	1-naphthyl		**5e**	59
6	**1f**	2-thienyl		**5f**	40
7	**1g**	cyclohexyl		**5g**	58[e]
8	**1h**	Et		**5h**	11[f]
9	**1a**	4-MeC_6H_4	TBICA	**6a**	70
10	**1b**	2-MeC_6H_4		**6b**	82
11	**1c**	4-$MeOC_6H_4$		**6c**	67
12	**1d**	phenyl		**6d**	63
13	**1e**	1-naphthyl		**6e**	30
14	**1f**	2-thienyl		**6f**	17
15	**1g**	cyclohexyl		**6g**	67

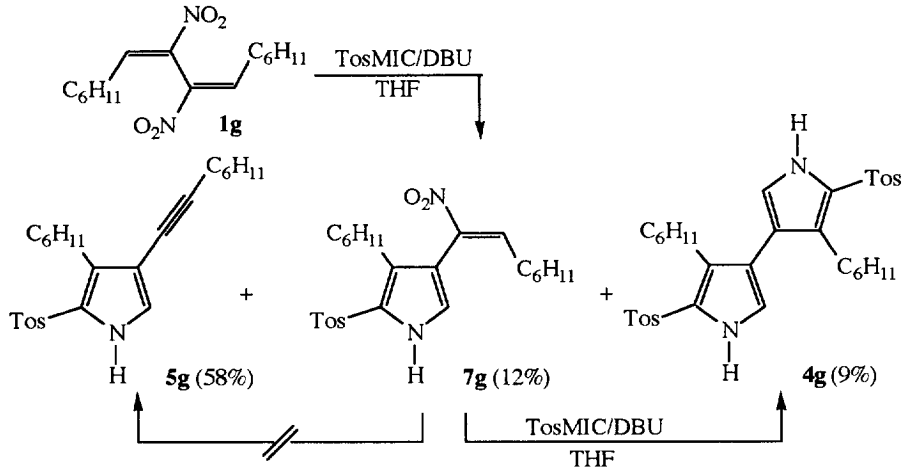
a) Tosylmethylisocyanide. b) *tert*-Butyl isocyanoacetate. c) Experiments were routinely carried out at room temperature under argon with a reaction time of 30 min with TosMIC and of 15 min with TBICA; [**1**] = 0.25 M, [isocyanide] = 0.27 M, [DBU] = 0.50 M. d) Unless otherwise stated, isolated yields after chromatography on silica gel column. e) Nitrovinylpyrrole **7g** (12%) and dipyrrole **4g** (9%) were also isolated (see Scheme 4). f) Yield estimated by ^1H NMR in mixed chromatographic fractions (see Experimental).

identical conditions. In agreement with such competitive decomposition of **1a-h** is also the fact that the lower the yield of either **5** or **6** the more unreacted isocyanide was recovered from the final reaction mixture. Particularly substantial was the quantity of tarry material formed in expt 8 of Table 4 (where 4,5-dinitro-3,5-octadiene **1h** was reacted with TosMIC/DBU) and consequently the corresponding pyrrole **5h** was isolated in very low yield in mixed (TosMIC) chromatographic fractions.

Last, but not least, it is interesting to note the behaviour observed with the 1,4-dicyclohexyl derivative **1g**, whose reactions with either TosMIC or TBICA give satisfactory yields of **5g** and **6g**, respectively. As shown in Scheme 4, moreover, it is intriguing that, only with TosMIC and unlike all the other cases examined, the formation of the ethynylpyrrole **5g** is accompanied by that of the nitrovinylpyrrole **7g** and of the 3,3'-dipyrrole **4g**. The latter compounds are the products expected (see introduction) on the grounds of an addition-cyclization-elimination process of the isocyanide (similar to that occurring on monofunctional 1-nitroalkenes)[2a] on a single or on both the nitrovinylic moieties of the dinitrobutadiene system.[9]

To gain insight into the mechanism leading to ethynylpyrroles **5** and **6** from dinitrobutadienes **1**, control experiments were performed on the pyrrole **7g**, which, by way of the residual nitrovinyl moiety, could in principle be the precursor of both **4g** (via a base-induced reaction with TosMIC) and **5g** (via a base-induced elimination of nitrous acid). Thus, **7g** was reacted (a) with TosMIC and DBU and (b) with DBU alone under typical reaction conditions. While the former experiment did afford the expected transformation of **7g** into **4g**, the latter reaction gave only decomposition products; in neither case the ethynylpyrrole **5g** could be detected

Scheme 4

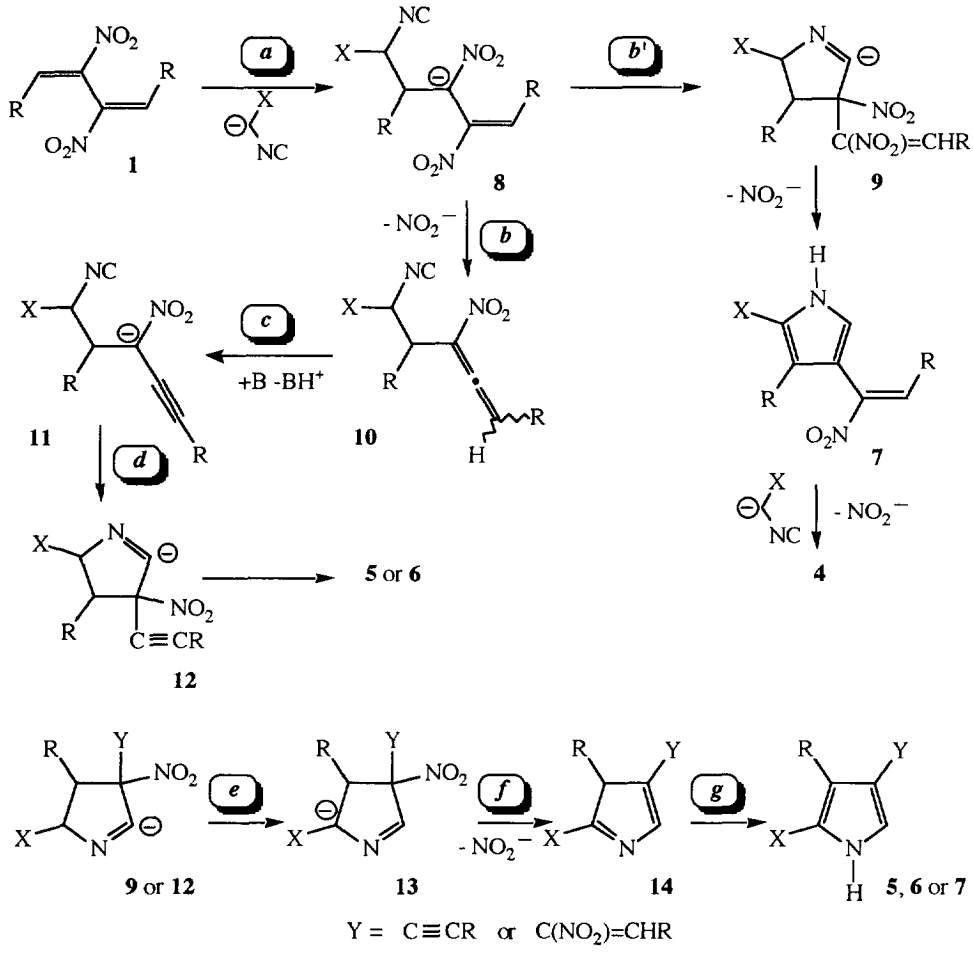


(TLC, ^{1}H NMR) in the final reaction mixtures. This outcome indicates that **7g** is not a precursor of **5g** and therefore suggests that in the route leading to ethynylpyrroles **5** or **6** from dinitrobutadienes **1** the formation of the carbon-carbon triple bond could precede that of the pyrrole ring.

Mechanistic hypotheses

On the grounds of the findings above, to explain the formation of the isolated products from dinitrobutadienes **1** the paths resumed in Scheme 5 can be envisaged. The first step of the overall process [step (a)] should involve attack of the isocyanide conjugate base to C-1 of the 2,3-dinitro-1,3-butadiene system with formation of the nitronate anion **8**. Step (a) is similar to that proposed for the analogous reactions on 1-nitroalkenes and, by analogy, an intramolecular cyclization to **9** [step (b')] would be expected. As reported below intermediates **9** would be the precursors of nitrovinylpyrroles **7** and hence of 3,3'-dipyrroles **4**. However, only in the case of the reaction of the dicyclohexyl derivative **1g** with TosMIC such kind of compounds have been isolated in the final reaction mixture and furthermore as by-products. Therefore, to rationalize the obtained results we speculate that in the studied reactions the main path open to the anionic adduct **8** involves [step (b)] a fast nitrite ion elimination to give a nitroallene intermediate **10**, which, under basic conditions, is converted [step (c)] into the propargyl nitronate **11**. Internal nucleophilic attack on the isocyano group [step (d)] will then give the cyclized anion **12** precursor of the isolated ethynylpyrroles **5** and **6**. In fact, it is very likely that the intermediates **12** are transformed [steps (e)-(g)] into the isolated products via a mechanism similar to that proposed for the analogous processes on 1-nitroalkenes and involving proton shift to **13**, vinylogous elimination of nitrite ion to **14** and aromatization to the corresponding pyrroles **5** and **6**. Finally a similar sequence of steps [(e)-(g)] can be envisaged to rationalize the formation, on a secondary route, of the isolated nitrovinylpyrrole **7g** from **9g** (X = Tos, R = C_6H_{11}) while a base-induced addition-cyclization-elimination process of TosMIC on the residual nitrovinyl moiety of **7g** can well account for the transformation of the latter into the likewise isolated by-product 3,3'-dipyrrole **4g**.

Scheme 5



Y = C≡CR or C(NO$_2$)=CHR

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were taken on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm).

Materials

Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C respectively. Tetrahydrofuran (THF) was purified by standard methods and distilled over potassium benzophenone ketyl radical before use. Analytical grade MeCN, DMF, DMSO and Pr^{i}OH were dried over molecular sieves (4Å) before use. Tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tosylmethylisocyanide (TosMIC) and *tert*-butyl isocyanoacetate (TBICA) were commercial products used as received. 1,4-Disubstituted 2,3-dinitro-1,3-butadienes **1a-h** were samples from our laboratory prepared as previously reported.[5c]

Reactions of 1,4-bis(4-methylphenyl)-2,3-dinitro-1,3-butadiene 1a with TosMIC in various base-solvent systems

Experiments 1-6 of Table 1.— Two millimoles of base (DBU or TMG) were slowly added, under argon and at 0 °C, to a magnetically stirred solution of TosMIC (0.39 g, 2 mmol) in 1 ml of solvent (see Table 1). Expt 3 in DMSO was initially carried out at ca. 15 °C. In every case, while stirring for 30 min, the mixture was left to reach room temperature and a solution of dinitrobutadiene **1a** (0.324 g, 1 mmol) in 3 ml of the same solvent was dropped into.

After the times reported in Table 1 the reaction mixtures were worked up as follows. For the experiments carried out in THF, the solvent was evaporated under reduced pressure in a rotary evaporator, while in the other cases the reaction mixtures were poured into brine and extracted with diethyl ether. The ether extracts were washed with brine, dried over sodium sulfate and evaporated under reduced pressure. In all the cases the residue was chromatographed on a silica gel column using dichloromethane as eluant to give 3-(4-methylphenyl)-4-[(4-methylphenyl)ethynyl]-2-[(4-methylphenyl)sulfonyl]pyrrole **5a** in the yields reported in Table 1. A substantial amount (0.8-0.9 mmol) of unreacted TosMIC, with *Rf* close to that of **5a**, was recovered in experiments 1-6.

Physical, spectroscopic and analytical data for **5a** are reported below together with those of the other pyrroles synthesized; a paragraph relevant to the *X*-ray crystallography of the same derivative **5a** is located at the end of this experimental section.

Experiment 7 of Table 1.— The reaction was carried out in THF using 1.1 mmol of TosMIC, 2 mmol of DBU and 1 mmol of **1a**. Such conditions afford the best yield of **5a**, furthermore coupled with an easier chromatographic isolation of the reaction product because of negligible quantities of unreacted TosMIC.

Reactions of dinitrobutadienes 1a-h with TosMIC or with TBICA.

The general procedure involved slow addition of 1 mmol of dinitrobutadiene **1a-h** dissolved in THF (3 ml) to a magnetically stirred solution, prepared as described above, of isocyanide (1.1 mmol) and DBU (2 mmol) in the same solvent (1 ml). The various experiments of Table 4 were routinely carried out under argon and at room temperature with reaction times of 30 or 15 minutes when TosMIC or TBICA were, respectively, used as reagents. The usual workup involved evaporation of the solvent under reduced pressure and chromatography of the crude on a silica gel column using dichloromethane as eluant. Essentially pure pyrroles **5a-g** and **6a-g** were thus obtained in the yields reported in Table 4.

In the reaction of the dicyclohexyl derivative **1g** with TosMIC (expt. 7 of Table 4) the chromatographic separation of the crude mixture furnished, after **5g**, two other products (eluted with dichloromethane-ether gradients) which were identified as 3-cyclohexyl-2-[(4-methylphenyl)sulfonyl]-4-(*E*)-[(1-nitro-2-cyclohexyl)-ethenyl]pyrrole **7** (12%) and 4,4'-dicyclohexyl-5,5'-bis[(4-methylphenyl)sulfonyl]-3,3'-dipyrrole **4g** (9%).

The reaction between 4,5-dinitro-3,5-octadiene **1h** and TosMIC gave **5h** in very low yields; the latter compound, moreover, could be identified only on the basis of its ^{1}H NMR absorptions in mixed chromatographic fractions; no analytically pure sample of **5h** could be obtained.

Pyrroles 5a-h and 6a-g

3-(4-Methylphenyl)-4-[(4-methylphenyl)ethynyl]-2-[(4-methylphenyl)sulfonyl]pyrrole **5a**: mp 176.9-177.7 °C (MeOH-H_2O) (Found: C, 76.3; H, 5.5; N, 3.2. $C_{27}H_{23}NO_2S$ requires: C, 76.2; H, 5.4; N, 3.3%); ^{1}H NMR ($CDCl_3$) δ 2.31 (3H, s), 2.33 (3H, s), 2.41 (3H, s), 7.05 (2H, AA' of AA'BB', *J* 8.1 Hz), 7.09 (2H, AA' of AA'BB', *J* 7.7 Hz), 7.18 (2H, AA' of AA'BB', *J* 8.4 Hz), 7.19 (2H, BB' of AA'BB', *J* 7.7 Hz), 7.20 (1H, d, *J* 3.2 Hz), 7.38 (2H, BB' of AA'BB', *J* 8.4 Hz), 7.40 (2H, BB' of AA'BB', *J* 8.1 Hz) and 9.45 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.42, 21.51, 81.51, 90.84, 108.67, 120.34, 124.34, 125.01, 126.89, 128.25, 128.38, 128.94, 129.38, 130.29, 131.09, 131.74, 137.64, 137.93, 138.62 and 143.96.

3-(2-Methylphenyl)-4-[(2-methylphenyl)ethynyl]-2-[(4-methylphenyl)sulfonyl]pyrrole **5b**: mp 145.4-146.2 °C (MeOH-H_2O) (Found: C, 76.1; H, 5.5; N, 3.2. $C_{27}H_{23}NO_2S$ requires: C, 76.2; H, 5.4; N, 3.3%); ^{1}H NMR ($CDCl_3$) δ 1.79 (3H, s), 1.92 (3H, s), 2.37 (3H, s), 7.07 (7H, m), 7.22 and 7.30 [6H in all, partly overlapped m and half AA'BB' system (*J* 8.4 Hz)], 9.46 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 19.63, 19.98,

21.55, 85.80, 89.79, 109.66, 123.10, 123.76, 125.09, 125.32, 125.72, 127.40, 127.80, 128.33, 129.24, 129.34, 129.41, 130.95, 131.20, 131.34, 131.45, 137.83, 138.18, 139.96 and 144.08.

3-(4-Methoxyphenyl)-4-[(4-methoxyphenyl)ethynyl]-2-[(4-methylphenyl)sulfonyl]pyrrole **5c**: mp 186.2-187.0 °C (MeOH-H_2O) (Found: C, 71.1; H, 5.1; N, 3.0. $C_{27}H_{23}NO_4S$ requires: C, 70.9; H, 5.1; N, 3.1%); ^1H NMR ($CDCl_3$) δ 2.33 (3H, s), 3.78 (3H, s), 3.87 (3H, s), 6.78 (2H, AA' of AA'BB', *J* 8.9 Hz), 6.92 (2H, AA' of AA'BB', *J* 8.9 Hz), 7.09 (2H, AA' of AA'BB', *J* 8.1 Hz), 7.19 (1H, d, *J* 3.2 Hz), 7.24 (2H, BB' of AA'BB', *J* 8.9 Hz), 7.36 (2H, BB' of AA'BB', *J* 8.1 Hz), 7.46 (2H, BB' of AA'BB', *J* 8.9 Hz) and 9.35 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.51, 55.30, 80.79, 90.71, 108.90, 113.17, 113.92, 115.62, 123.73, 124.40, 125.04, 126.91, 129.40, 131.75, 132.66, 138.68, 143.97, 159.39 and 159.46.

2-[(4-Methylphenyl)sulfonyl]-3-phenyl-4-(phenylethynyl)pyrrole **5d**: mp 165.7-166.2 °C (MeOH-H_2O) (Found: C, 75.3; H, 4.9; N, 3.6. $C_{25}H_{19}NO_2S$ requires: C, 75.5; H, 4.8; N, 3.5%); ^1H NMR ($CDCl_3$) δ 2.32 (3H, s), 7.07 (2H, AA' of AA'BB', *J* 8.0 Hz), 7.25 (6H, m), 7.37 (5H, m), 7.50 (2H, m) and 9.55 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.52, 82.13, 90.81, 108.53, 123.36, 124.70, 125.36, 126.94, 127.67, 127.85, 127.97, 128.18, 129.38, 130.48, 131.15, 131.21, 131.66, 138.36 and 144.10.

2-[(4-Methylphenyl)sulfonyl]-3-(1-naphthyl)-4-(1-naphthylethynyl)pyrrole **5e**: mp 203.0-204.0 °C (MeOH) (Found: C, 79.4; H, 4.7; N, 2.8. $C_{33}H_{23}NO_2S$ requires: C, 79.6; H, 4.7; N, 2.8%); ^1H NMR ($CDCl_3$) δ 2.16 (3H, s), 6.75 (3H, m), 6.90 (1H, m), 7.26 (9H, m), 7.56 (4H, m), 7.89 (1H, d, *J* 8.2 Hz), 7.97 (1H, dd, *J* 1.8 and 7.8 Hz) and 9.59 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.33, 86.67, 89.46, 110.45, 120.74, 123.74, 124.90, 125.16, 125.54, 125.77, 125.84, 125.97, 126.25, 127.24, 127.75, 127.82, 128.09, 128.72, 129.00, 129.18, 129.62, 129.97, 132.25, 132.77, 132.80, 133.34, 137.35 and 143.90.

2-[(4-Methylphenyl)sulfonyl]-3-(2-thienyl)-4-(2-thienylethynyl)pyrrole **5f**: mp 158.2-159.0 °C (petroleum ether-toluene) (Found: C, 61.4; H, 3.8; N, 3.4. $C_{21}H_{15}NO_2S_3$ requires: C, 61.6; H, 3.7; N, 3.4%); ^1H NMR ($CDCl_3$) δ 2.34 (3H, s), 6.96 (1H, dd, *J* 3.6 and 5.1 Hz), 7.12 (4H, m), 7.23 [2H in all, partly overlapped d (*J* 3.2 Hz) and dd (*J* 1.1 and 5.1 Hz)], 7.37 (1H, dd, *J* 1.1 and 5.1 Hz), 7.47 (2H, half AA'BB' system, *J* 8.0 Hz), 7.53 (1H, dd, *J* 1.1 and 3.6 Hz) and 9.36 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.57, 85.33, 85.61, 108.55, 123.30, 124.11, 124.76, 125.52, 126.83, 126.91, 126.98, 127.11, 129.51, 129.65, 131.19, 131.56, 137.84 and 144.38.

3-Cyclohexyl-4-(cyclohexylethynyl)-2-[(4-methylphenyl)sulfonyl]pyrrole **5g**: mp 139.4-140.5 °C (MeOH-H_2O) (Found: C, 73.2; H, 7.8; N, 3.5. $C_{25}H_{31}NO_2S$ requires: C, 73.3; H, 7.6; N, 3.4%); ^1H NMR ($CDCl_3$) δ 1.35 (10H, m), 1.85 (10H, m), 2.40 (3H, s), 2.55 (1H, m), 3.03 (1H, tt, *J* 3.4 and 12.1 Hz), 6.97 (1H, d, *J* 3.1 Hz), 7.26 and 7.73 (2H each, AA'BB', *J* 8.1 Hz) and 9.07 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.55, 24.89, 25.94, 26.02, 26.78, 29.81, 30.65, 32.64, 35.73, 73.71, 96.57, 107.26, 123.41, 125.89, 126.73, 129.71, 136.32, 139.86 and 143.86.

4-(1-Butyn-1-yl)-3-ethyl-2-[(4-methylphenyl)sulfonyl]pyrrole **5h**: as stated above, no analytically pure sample of this product could be obtained; **5h** was isolated in chromatographic fractions mixed with unreacted TosMIC and identified only on the grounds of the following ^1H NMR absorptions: ($CDCl_3$) δ 1.06 (3H, t, *J* 7.5 Hz), 1.19 (3H, t, *J* 7.5 Hz), 2.37 [5H, s overlapped with q (*J* 7.5 Hz)], 2.68 (2H, q, *J* 7.5 Hz), 6.98 (1H, d, *J* 3.1 Hz), 7.27 and 7.75 (2H each, AA'BB', *J* 8.1 Hz) and 9.12 (1H, br s).

2-tert-Butoxycarbonyl-3-(4-methylphenyl)-4-[(4-methylphenyl)ethynyl]pyrrole **6a**: mp 195.3-196.0 °C (MeOH-H_2O) (Found: C, 80.6; H, 7.0; N, 3.7. $C_{25}H_{25}NO_2$ requires: C, 80.8; H, 6.8; N, 3.8%); ^1H NMR ($CDCl_3$) δ 1.43 (9H, s), 2.32 (3H, s), 2.39 (3H, s), 7.07 (2H, half AA'BB' system, *J* 8.1 Hz), 7.17, 7.21 and 7.23 [5H in all, d (*J* 3.1 Hz) and two halves of AA'BB' systems (*J* ca. 8.1 Hz) partly overlapped], 7.50 (2H, half AA'BB' system, *J* 8.1 Hz) and 9.15 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.35, 21.43, 28.24, 81.54, 82.81, 90.17, 107.69, 120.03, 120.84, 124.59, 127.93, 128.93, 130.29, 130.44, 131.04, 132.35, 136.68, 137.59 and 160.39.

2-tert-Butoxycarbonyl-3-(2-methylphenyl)-4-[(2-methylphenyl)ethynyl]pyrrole **6b**: mp 178.6-180.0 °C (MeOH-H_2O) (Found: C, 80.9; H, 6.7; N, 3.9. $C_{25}H_{25}NO_2$ requires: C, 80.8; H, 6.8; N, 3.8%); ^1H NMR ($CDCl_3$) δ 1.26 (9H, s), 1.98 (3H, s), 2.20 (3H, s), 7.07 (3H, m), 7.22 (6H, m) and 9.69 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 20.09, 27.93, 81.02, 87.09, 88.97, 108.26, 121.03, 123.53, 124.25, 124.88, 125.25,

127.18, 127.47, 129.15, 129.19, 130.33, 131.09, 132.63, 134.45, 136.88, 139.91 and 160.79.

2-tert-Butoxycarbonyl-3-(4-methoxyphenyl)-4-[(4-methoxyphenyl)ethynyl]pyrrole **6c**: mp 197.1-197.8 °C (MeOH-H_2O) (Found: C, 74.1; H, 6.2; N, 3.4. $C_{25}H_{25}NO_4$ requires: C, 74.4; H, 6.2; N, 3.5%); ^1H NMR ($CDCl_3$) δ 1.44 (9H, s), 3.79 (3H, s), 3.85 (3H, s), 6.80 (2H, AA' of AA'BB', *J* 8.9 Hz), 6.94 (2H, AA' of AA'BB', *J* 8.8 Hz), 7.15 (1H, d, *J* 3.2 Hz), 7.29 (2H, BB' of AA'BB', *J* 8.9 Hz), 7.55 (2H, BB' of AA'BB', *J* 8.8 Hz) and 9.32 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 28.30, 55.26, 81.52, 82.07, 89.92, 107.78, 112.72, 113.87, 116.09, 119.90, 124.44, 125.83, 131.79, 132.00, 132.56, 158.82, 159.16 and 160.45.

2-tert-Butoxycarbonyl-3-phenyl-4-(phenylethynyl)pyrrole **6d**: mp 154.5-155.7 °C (MeOH-H_2O) (Found: C, 80.5; H, 6.3; N, 4.0. $C_{23}H_{21}NO_2$ requires: C, 80.4; H, 6.2; N, 4.1%); ^1H NMR ($CDCl_3$) δ 1.41 (9H, s), 7.32 (9H, m), 7.59 (2H, m) and 9.26 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 28.21, 81.67, 83.48, 90.16, 107.64, 120.35, 123.90, 124.71, 127.12, 127.22, 127.56, 128.17, 130.64, 131.12, 132.44, 133.50 and 160.57.

2-tert-Butoxycarbonyl-3-(1-naphthyl)-4-(1-naphthylethynyl)pyrrole **6e**: mp 193.5-194.3 °C (MeOH-H_2O) (Found: C, 83.9; H, 5.6; N, 3.1. $C_{31}H_{25}NO_2$ requires: C, 83.9; H, 5.7; N, 3.2%); ^1H NMR ($CDCl_3$) δ 0.99 (9H, s), 7.09 (1H, m), 7.37 (7H, m), 7.63 (4H, m), 7.90 (3H, m) and 9.86 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 27.60, 77.22, 81.12, 88.14, 88.66, 109.23, 121.38, 122.39, 124.64, 125.02, 125.15, 125.47, 125.64, 126.04, 126.25, 126.30, 126.68, 127.62, 127.82, 127.93, 128.13, 129.09, 130.73, 132.68, 132.95, 133.00, 133.62 and 160.74.

2-tert-Butoxycarbonyl-3-(2-thienyl)-4-(2-thienylethynyl)pyrrole **6f**: mp 154.5-155.2 °C (petroleum ether) (Found: C, 64.0; H, 4.7; N, 4.0. $C_{19}H_{17}NO_2S_2$ requires: C, 64.2; H, 4.8; N, 3.9%); ^1H NMR ($CDCl_3$) δ 1.51 (9H, s), 6.96 (1H, dd, *J* 3.7 and 5.1 Hz), 7.08 (1H, dd, *J* 3.7 and 5.1 Hz), 7.18 (2H, app. d, *J* 3.3 Hz), 7.23 (1H, dd, *J* 1.1 and 5.1 Hz), 7.36 (1H, dd, *J* 1.1 and 5.1 Hz), 7.49 (1H, dd, *J* 1.1 and 3.7 Hz) and 9.14 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 28.26, 82.10, 84.37, 87.02, 107.62, 120.40, 123.83, 124.75, 124.96, 125.63, 126.22, 126.69, 126.92, 128.62, 131.16, 133.66 and 159.97.

2-tert-Butoxycarbonyl-3-cyclohexyl-4-(cyclohexylethynyl)pyrrole **6g**: mp 141.9-143.3 °C (MeOH-H_2O) (Found: C, 77.9; H, 9.6; N, 3.8. $C_{23}H_{33}NO_2$ requires: C, 77.7; H, 9.4; N, 3.9%); ^1H NMR ($CDCl_3$) δ 1.35 (10H, m), 1.57 (9H, s), 1.95 (10H, m), 2.59 (1H, m), 3.41 (1H, tt, *J* 3.4 and 12.1 Hz), 6.09 (1H, d, *J* 3.1 Hz) and 8.85 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 24.97, 26.07, 26.29, 27.26, 28.53, 29.97, 31.41, 32.82, 36.12, 74.90, 81.06, 95.57, 106.53, 119.20, 125.01, 138.01 and 160.92.

Nitrovinylpyrrole 7g and 3,3'-dipyrrole 4g.

3-Cyclohexyl-2-[(4-methylphenyl)sulfonyl]-4-(E)-[(1-nitro-2-cyclohexyl)ethenyl]pyrrole **7g**: mp 194.2-195.3 °C (MeOH-H_2O) (Found: C, 66.0; H, 7.3; N, 6.0. $C_{25}H_{32}N_2O_4S$ requires: C, 65.8; H, 7.1; N, 6.1%); ^1H NMR ($CDCl_3$) δ 1.20 (10H, m), 1.65 (10H, m), 2.16 (1H, m), 2.43 (3H, s), 2.90 (1H, m), 6.84 (1H, d, *J* 3.1 Hz), 7.18 (1H, d, *J* 10.7 Hz), 7.31 and 7.79 (2H each, AA'BB', *J* 8.2 Hz) and 9.55 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 21.60, 24.93, 25.55, 25.82, 26.88, 31.55, 32.12, 36.58, 38.36, 113.77, 123.96, 125.03, 127.00, 129.84, 134.44, 139.58, 144.25, 144.84 and 145.18.

4,4'-Dicyclohexyl-5,5'-bis[(4-methylphenyl)sulfonyl]-3,3'-dipyrrole **4g**: mp 280 °C (decomposition) (AcOEt) (Found: C, 67.2; H, 6.7; N, 4.4. $C_{34}H_{40}N_2O_4S_2$ requires: C, 67.5; H, 6.7; N, 4.6%); ^1H NMR ($CDCl_3$) δ 1.30 (20H, m), 2.40 (6H, s), 2.75 (2H, m), 6.73 (2H, d, *J* 3.0 Hz), 7.26 and 7.71 (4H each, AA'BB', *J* 8.2 Hz) and 9.26 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 21.55, 25.89, 26.94, 32.66, 36.63, 119.12, 123.22, 123.41, 126.68, 129.55, 134.77, 140.59 and 143.63.

Control experiments

Treatment of the nitrovinylpyrrole 7g with DBU.— A solution of compound **7g** (46 mg, 0.1 mmol) and DBU (17 mg, 0.11 mmol) in 1 ml of THF was kept at room temperature and under magnetic stirring following the progress of the reaction by TLC. Neither TLC nor the ^1H NMR spectrum of the crude reaction mixture (obtained by the usual workup after 24 h) showed formation of the ethynylpyrrole **5g**. The reaction instead furnished a complex mixture containing also some unreacted **7g**.

Treatment of the nitrovinylpyrrole 7g with DBU and TosMIC.— The nitrovinylpyrrole **7g** (46 mg, 0.1 mmol), dissolved in 0.5 ml of THF, was added (magnetic stirring, room temperature, under argon) to a solution of DBU (17 mg, 0.11 mmol) and TosMIC (21 mg, 0.11 mmol) in 0.5 ml of THF. The progress of the reaction was followed by TLC and, after 24 h, the mixture was worked up as usually. No trace of ethynylpyrrole **5g** could be detected by TLC and ^{1}H NMR analysis of the crude reaction product. The latter was chromatographed on a silica gel column eluting with gradients of light petroleum-diethyl ether to give 36 mg (60%) of 3,3'-dipyrrole **4g**.

X-ray crystallography of compound 5a.

Yellow trasparent crystals were obtained from solution in methanol. After preliminary Laue photographs a crystal was mounted on a four-circle diffractometer; data were collected using graphite-monochromated Mo-Kα radiation. Experimental conditions, crystal data and refinement parameters are summarized in Table 5. During the data collection the centering of five reflections was repeated every 250 measurements to test the crystal orientation. Two reflections were monitored every 90 min to check the crystal stability; no decay was observed. Collected data were corrected for Lorentz, polarization and absorption[10] effects.

The structure was solved by direct methods using the *NRCVAX* system of programs.[11] After some trials, after which the cutoff value of | E | was lowered to 1.1 and the number of reflections in the starting set increased, the fourth 'best' E-map allowed to recognize 29 of the 31 heavy atoms; two methyl carbon atoms were then located by a difference map.

The refinement was accomplished on F^2 data by means of isotropic, and then anisotropic full-matrix least squares with the program *SHELXL93*.[12] During the refinement all the hydrogen atoms, except those of the methyl groups, were recognized on difference maps and refined as isotropic. Methyl hydrogens are affected by partial rotational disorder; an attempt to locate them was performed by means of a circular difference synthesis calculated for each group at a fixed C-H distance (0.96 Å) and a fixed C-C-H angle (109.47°). For each methyl group, the rotation angle and a common U(H) thermal factor were refined. Notwithstanding the high final values of these thermal parameters the refinement converged well, with a maximum shift-to-e.s.d. ratio 0.074 for the rotation angle of methyl C(14).

Table 5. Crystal data and structure refinement for **5a**.

Formula	$C_{27}H_{23}NO_2S$	Scan mode	ω/θ
Formula weight	425.52	Scan width, scan speed	1.05°, 1 → 16 °/min
Temperature	293 K	θ range (data coll.)	2.5 → 25°
Wavelenght	0.71070 Å	Index ranges	h 0 → 11
Space group	$P\bar{1}$		k -12 → 12
Unit cell dimension	a = 9.910(9) Å α = 94.56(4)°		l -14 → 13
	b = 10.231(6) Å β = 101.41(6)°	Reflections collected	4041
	c = 11.854(6) Å γ = 98.54(6)°	Independent reflections	4041
Volume	1157.7(14) Å^3	Refinement method	Full-matrix least-squares on F^2
Z	2		
θ range (cell param.)	13.5 → 17.7°	Data/parameters	4041/342
Density (calcd.)	1.221 g cm^{-3}	Max. shift/error	0.074
Crystal size	0.44 x 0.40 x 0.12 mm	Goodness-of-fit on F^2	1.015
Absorpt. coeff.	0.163 mm^{-1}	R index on F [F>4σ(F)]	R1 = 0.0435 on 2852 reflections
Transm. factors	0.901 → 0.999		
F(000)	448	R index on F^2	wR2 = 0.1171 on 4041 reflections
Diffractometer	Enraf Nonius CAD-4		

The weighting scheme was $w = [\sigma^2(F_O^2) + (0.066P)^2 + 0.02P]^{-1}$, with $\sigma(F_O^2)$ from the counting statistics and $P = (F_O^2 + 2F_c^2)/3$. Final reliability factors were *R1* = 0.0435 on 2852 $F_O > 4\,\sigma(F_O)$ and *wR2* = 0.1171 on all 4041 F_O^2 data, with a goodness of fit *S* = 1.015. The largest correlation matrix element was 0.509. The final difference Fourier map was essentially flat, the electron density ranging between 0.187 and -0.192 e Å^{-3}.

Scattering factors were taken from *SHELXL93*. Geometry calculations were performed with the program *PARST93*;[13] Figure 1 was obtained using *ORTEP*.[14]

Tables of atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, Lensfield Rd., Cambridge, CB2 1EW, U.K.

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