

# Conformational studies of substituted nitroanilines: geometry of 2-methyl-5-nitroaniline

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The title compound (C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>), is monoclinic, space group P2<sub>1</sub>/n, with  $a = 9.552(2)$ ,  $b = 5.677(2)$ ,  $c = 13.586(3)$  Å,  $\beta = 92.68(2)^\circ$ , and  $D_x = 1.374$  g·cm<sup>-3</sup> for  $Z = 4$ . The refinement converged to  $R = 0.043$ ,  $wR = 0.038$ . The molecule is approximately planar, with dihedral angles of  $3.7(2.1)^\circ$  between the amino group and the aromatic ring, and  $3.2(2)^\circ$  between the nitro group and the ring. According to the UV spectrum in solution, the molecular geometry indicates weak intramolecular charge transfer. The three-dimensional structure is stabilized by three intermolecular H bonds. A bifurcated one induces the formation of chains along [101], while the other two link molecules that belong to adjacent chains and are related by an inversion center.

**KEY WORDS:** Nitroaniline derivatives; 2-methyl-5-nitroaniline; nonlinear optic; spectroscopic study; structure determination; hydrogen bonds.

## Introduction

Tailoring materials with nonlinear optical response, e.g., second harmonic generation (SHG), has been the aim of several studies of nitroaniline derivatives. It has been found that weak hydrogen bonds seem to determine the molecular organization of these compounds.<sup>1-3</sup> The authors propose that N-H...O interactions, with specific geometries and lengths exceeding the sum of the Van der Waals radii, are responsible for the formation of polar chains not only in solid state but also in solution.<sup>1</sup> Therefore, the appropriate packing of these chains would lead to the acentric crystals required for SHG.

The present study intends to add to the understanding of the parameters that govern the molecular aggregation and the macroscopic properties of nitroanilines. The 2-methyl-4-nitroaniline (MNA) is an isomer of the title compound (M5NA) that shows strong conjugative effects. It also exhibits an exceptionally large

linear electro-optic effect<sup>4</sup> and second harmonic coefficient.<sup>5</sup> Conjugative effects in M5NA are expected to be smaller than in MNA, but larger than in the *meta*-nitroaniline (*m*-NA), which presents a low efficiency for second harmonic generation (SHG). Because of the known structural results for both aforementioned anilines, MNA<sup>4</sup> and *m*-NA,<sup>6</sup> we expected that M5NA would crystallize in a noncentrosymmetric space group and SHG would be observed. Tests done on powder samples did not show nonlinear second order effects.<sup>7</sup> To rationalize this result, an X-ray single crystal structure determination was undertaken and UV data for M5NA and MNA in solution were obtained.

## Experimental

The UV spectra were recorded on a Shimadzu UV-240 Spectrophotometer with a band width of 2nm. A well-shaped crystal obtained by slow evaporation from acetone was chosen for X-ray study. Crystal data and data collection and refinement details are shown in Table 1. Atomic parameters are given in Table 2.

The structure was solved by direct methods with *SHELXS86*.<sup>8</sup> The model obtained was refined by full-

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**Table 1.** Crystal data and structure refinement,<sup>a</sup> esd's in parentheses

Crystal data	
Compound: C <sub>7</sub> N <sub>2</sub> O <sub>2</sub> H <sub>8</sub>	Mo K $\alpha$
$M_r = 152.15$	$\lambda = 0.71073 \text{ \AA}$
Space group: Monoclinic, P2 <sub>1</sub> /n	$\mu = 0.64 \text{ mm}^{-1}$
Cell constants:	T = 295 K
$a = 9.552(2) \text{ \AA}$	Size: $0.125 \times 0.15 \times 0.25 \text{ mm}$
$b = 5.677(2) \text{ \AA}$	Color: yellow
$c = 13.586(3) \text{ \AA}$	Crystal source: purify from commercial product: Janssen
$\beta = 92.68(2)^\circ$	Cell parameters from: 20 reflections with $\theta = 0\text{--}25^\circ$
$V = 735.7(11) \text{ \AA}^3$	
$Z = 4$	
$D_x = 1.374 \text{ g-cm}^{-3}$	
Data collection	
Enraf-Nonius CAD-4 Diffractometer	$\theta_{\max} = 25^\circ$
$\theta/2\theta$ Scans	$h = -11 \rightarrow 11$
1071 Measured reflections	$k = 0 \rightarrow 6$
1071 Independent reflections	$l = 0 \rightarrow 16$
602 Observed reflection	1 Standard reflc. ( $\bar{1}, 3, 2$ )
469 Unobserved reflection if $I < 3.0 \sigma(I)$	Frequency: 100 min
Corrections: lorentz and polarization	Intensity variation: 3%
Refinement	
Refinement on F	$w = 1.8305/[\sigma^2(F_o) + 5 \times 10^{-5} F_o^2]$
Final R = 0.043	$(\Delta/\sigma)_{\max} = 0.012$
$wR = 0.038$	$\Delta\rho_{\max} = 0.15 \text{ e \AA}^{-3}$
$S = 2.25$	$\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
602 Reflections	Atomic scattering factors from International Tables, Vol. IV, Table 2.2B
119 parameters	

<sup>a</sup> Data collection: CAD-4 (Enraf Nonius)<sup>13</sup> software 1990. Cell refinement: CAD-4 (Enraf-Nonius) software 1990. Data reduction: MoLEN.<sup>13</sup> Calculations were carried out on a micro VAXII system using the programs: PLUTO,<sup>10</sup> ORTEP-III<sup>11</sup> and PARST.<sup>12</sup>

matrix least-squares procedure by means of SHELX76.<sup>9</sup>

## Discussion

### Molecular geometry

The aromatic ring is essentially planar, showing a small value of The Total Puckering Amplitude,<sup>14</sup> QT = 0.014(4). Unlike MNA and *m*-NA, where the amino groups are twisted out of the phenyl ring, 21.5(1) and 32.0(1) $^\circ$  respectively, the amino group in M5NA is coplanar with the aromatic ring, 3.7(2.1) $^\circ$ , within the experimental error. On the other hand, the nitro group

**Table 2.** Atomic coordinates and equivalent isotropic displacement parameters, esd's in parentheses

$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* \cdot a_j^* \cdot a_i \cdot a_j$				
Atom	$x/a$	$y/b$	$z/c$	$U_{eq}$
C(1)	1.0040(4)	0.1869(7)	0.2932(2)	0.0386(15)
C(2)	0.9620(4)	-0.0205(7)	0.2425(3)	0.0396(14)
C(3)	0.8685(4)	-0.1707(7)	0.2854(3)	0.0455(15)
C(4)	0.8136(4)	-0.1272(7)	0.3755(3)	0.0449(16)
C(5)	0.8542(4)	0.0781(7)	0.4221(3)	0.0384(14)
C(6)	0.9481(4)	0.2350(7)	0.3842(3)	0.0386(15)
C(7)	1.0164(4)	-0.0718(7)	0.1425(3)	0.0585(16)
N(1)	1.0990(4)	0.3380(7)	0.2548(3)	0.0631(16)
N(2)	0.7932(4)	0.1379(7)	0.5161(2)	0.0492(14)
O(1)	0.7059(3)	0.0083(6)	0.5485(2)	0.0831(15)
O(2)	0.8321(3)	0.3167(6)	0.5594(2)	0.0701(14)

displays a dihedral angle of 3.2(2) $^\circ$  with the mean ring plane. This value coincides with that observed in *m*-NA, but is larger than the one found in MNA, 1.04(15) $^\circ$

The bond length C(1)–N(1), 1.369(6) $\text{\AA}$ , is shorter than in *m*-NA, 1.391(3) $\text{\AA}$ ,<sup>6</sup> and larger than in MNA, 1.353(3) $\text{\AA}$ ,<sup>4</sup> and in other conjugated 4-nitroanilines like *p*-nitroaniline, 1.356(3) $\text{\AA}$ ,<sup>15</sup> and N,N-dimethyl-*p*-nitroaniline, 1.35(8) $\text{\AA}$ .<sup>16</sup> This indicates that the degree of conjugation between the amino and the nitro groups in M5NA is smaller than in the mentioned 4-nitroanilines. The bond C(5)–N(2), 1.468(5) $\text{\AA}$ , is larger than the C(4)–N(2) bond presented for the MNA, 1.422(3) $\text{\AA}$ , and similar to the value observed in *m*-NA, 1.467(4) $\text{\AA}$ , and to the mean value, 1.471(2) $\text{\AA}$ , reported by Domenicano *et al.*<sup>17</sup> for the C–N bond length in nitrobenzene derivatives for which the substituents were chosen to avoid the conjugation. The C–Me bond length, C(2)–C(7) = 1.505(6) $\text{\AA}$  is in agreement with the value presented for the MNA, 1.507(3) $\text{\AA}$ .

The N–O bonds, N(2)–O(1) 1.210(5) $\text{\AA}$  and N(2)–O(2) 1.222(5) $\text{\AA}$ , agree with the mean value, 1.218(11) $\text{\AA}$ , obtained from 334 nitrobenzene derivatives surveyed from the 1987 version of the CSD.<sup>18</sup> The bond angle O(1)–N(2)–O(2), 121.9(3) $^\circ$ , is smaller than the mean values 123.7(9) $^\circ$ <sup>18</sup> but larger than the average, 118.9 $^\circ$ , obtained from 44 nitroanilines NO<sub>2</sub> groups involved in hydrogen bonds.<sup>1</sup>

The bond lengths corrected by thermal vibration,<sup>12</sup> Table 3, do not show departure from the trends described above.

### Influence of the substituents

The additivity of the effect of the substituents on the ring geometry was analyzed using the angular

**Table 3.** Bond lengths (Å), esd's in parentheses, thermal vibration corrections in brackets

C(1)–C(2)	1.412(5)[1.414]	C(1)–N(1)	1.369(6)[1.397]
C(2)–C(3)	1.383(6)[1.388]	C(2)–C(7)	1.505(6)[1.524]
C(3)–C(4)	1.376(6)[1.377]	C(4)–C(5)	1.373(6)[1.381]
C(5)–C(6)	1.380(6)[1.380]	C(5)–N(2)	1.468(5)[1.477]
C(6)–C(1)	1.396(5)[1.396]	N(2)–O(1)	1.210(5)[1.257]
N(2)–O(2)	1.222(5)[1.253]		

Bond angles (°), esd's in parentheses			
C(1)–C(2)–C(7)	119.9(3)	C(1)–C(2)–C(3)	118.8(3)
C(5)–C(6)–C(1)	119.0(4)	C(6)–C(1)–N(1)	120.1(3)
C(6)–C(1)–C(2)	118.8(3)	C(2)–C(1)–N(1)	120.9(3)
C(2)–C(3)–C(4)	123.0(4)	C(3)–C(2)–C(7)	121.1(4)
C(4)–C(5)–N(2)	118.8(3)	C(5)–C(4)–C(3)	116.8(4)
C(6)–C(5)–N(2)	117.8(3)	C(6)–C(5)–C(4)	123.3(4)
C(5)–N(2)–O(2)	119.1(3)	C(5)–N(2)–O(1)	118.9(3)
O(1)–N(2)–O(2)	121.9(3)		

parameters of Domenicano and Murray-Rust (DMR),<sup>19</sup> Table 4. To get a better understanding of the results obtained, the additivity of the effect of the substituents in MNA and *m*-NA was also analyzed and included in Table 4.

It can be seen from the value of the nonadditivity parameters (NAP),<sup>20</sup> that additivity is accomplished in *m*-NA. For both M5NA and MNA the NAP parameter is less than 3σ, NAP 3.0 (1.7) and 4.4 (1.52) respectively. This would indicate that the additivity of the effects of the substituents is also attained in both compounds, within experimental error. However, the validity of this hypothesis is weaker for MNA. These results are consistent with the different degree of intramolecular charge transfer between the donor and the acceptor groups expected from their relative location and confirmed by UV data, shown below.

## UV spectra

Highly conjugated nitroanilines exhibit an intense band at about 375 nm. It can be assigned to an intramolecular charge transfer (CT) band due to a transition accompanied with a partial electron transfer from the electron-donating amino group to the electron-accepting nitro group through the π system of the benzene ring.<sup>21</sup> Figure 1 and Table 5 show that MNA presents a strong band at 374 nm, while the intensity of this band, positioned at 370 nm, drops in M5NA. As mentioned above, these results agree with the relative location of the amino and nitro substituents in both compounds.

The MNA spectrum shows a second band at 224 nm. This can be assigned to the benzene π → π\* transition modified by the amino group. The third band at 204 nm, and the shoulder at 260 nm, display the bathochromic effect of the alkyl substituent on the spectrum at benzene.<sup>21</sup>

The spectrum at M5NA displays two intense bands at 251 and 229 nm. They can be interpreted as benzene π → π\* transition modified by the nitro and amine substituents respectively. Further analysis of the M5NA spectrum shows a weaker band at 286 nm, probably arising from an electronic transition involving the methyl and nitro substituents.

The comparison of the present UV results with that found in the literature for *m*-NA (Table 5) confirms our previous assumption on the relative magnitude of the conjugative effects in the three compounds.

## Crystal packing

The molecules of M5NA exhibit a centrosymmetric arrangement. Figure 2 displays the intermolecular

**Table 4.** Experimental and calculated endocyclic angles, and non-additivity parameter values, esd's in parentheses

θ <sub>i</sub>	ANGLES (°)	2-Methyl-5-nitro		<i>m</i> -Nitroaniline		2-Methyl-4-nitro	
		D.M.R. <sup>a</sup>	Exper.	D.M.R.	Exper.	D.M.R.	Exper.
θ <sub>1</sub>	C(6)–C(1)–C(2)	120.1(4)	118.8(3)	118.9(2)	119.1(3)	120.2(5)	119.3(2)
θ <sub>2</sub>	C(1)–C(2)–C(3)	118.7(5)	118.8(3)	118.3(3)	118.3(2)	118.6(4)	119.0(2)
θ <sub>3</sub>	C(2)–C(3)–C(4)	122.3(3)	123.0(3)	124.0(3)	123.9(3)	120.1(3)	120.8(2)
θ <sub>4</sub>	C(3)–C(4)–C(5)	117.2(4)	116.8(3)	116.9(2)	116.8(3)	122.0(5)	120.7(2)
θ <sub>5</sub>	C(4)–C(5)–C(6)	123.1(5)	123.3(3)	121.0(3)	121.3(2)	118.3(4)	119.1(2)
θ <sub>6</sub>	C(5)–C(6)–C(1)	118.7(3)	119.0(3)	120.9(3)	120.6(3)	120.9(3)	121.2(2)
	N.A.P. <sup>b</sup>	3.0 (σ = 1.7)		1.0 (σ = 1.7)		4.4 (σ = 1.5)	

<sup>a</sup> Domenicano and Murray-Rust.<sup>19</sup>

<sup>b</sup> N.A.P. =  $\sum |\theta_{\text{exp.}} - \theta_{\text{calc.}}|$ ; θ: endocyclic angles.  $\sigma = [\sum (\sigma_{\text{calc.}} + \sigma_{\text{exp.}})^2]^{1/2}$ .

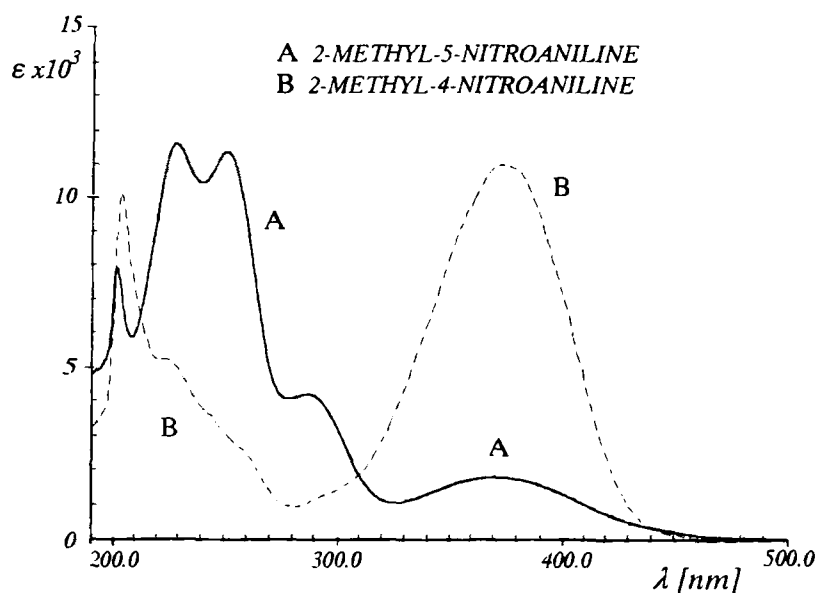


Fig. 1. MNA and M5NA UV spectra.

hydrogen bonding scheme and the atom labels. As expected after Panunto *et al.*,<sup>1</sup> an amino proton is situated between both oxygens of the nitro group. This induces the formation of infinite chains with three center interactions along the  $[10\bar{1}]$  direction. The second amino proton, not locked in the interactions that give rise to the chains, is involved in a two center

(TC) bond with a molecule of a neighboring chain. This interaction induces centrosymmetric dimers.

Molecular orbital modeling of monomeric *p*- and *m*-nitroaniline aggregates, using AM1 semiempirical molecular orbital methods, has shown that TC hydrogen bonds are the optimal interactions.<sup>23</sup> This seems to contradict the Panunto *et al.* finding<sup>1</sup> and our present

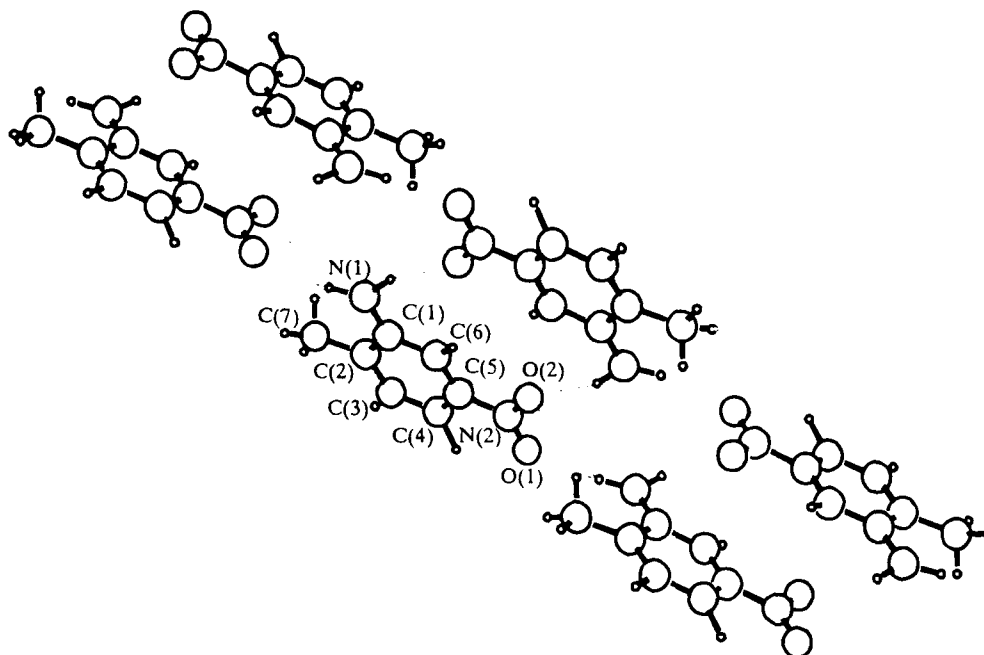


Fig. 2. Drawing of the crystal packing showing the intermolecular hydrogen bonds scheme and the atom labels.

Table 5. UV spectral bands of M5NA, MNA and *m*-Na

Compound	First band		Second band		Third band		Fourth band		Fifth band	
	$\lambda_{\max}^*$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$	$\lambda_{\max}$	$\epsilon_{\max}$
2-Me-5-NA <sup>a</sup>	370	1.775	286	4.151	251	11.147	229	11.372	202	7.685
2-Me-4-NA <sup>a</sup>	374	11.108	260	2.337	242	3.565	224	4.821	204	9.508
<i>m</i> -NA <sup>b</sup>	370	1.349	275	3.981	235	17.378	—	—	—	—

\*  $\lambda_{\max}$  in nm; <sup>a</sup>This work; <sup>b</sup>Passeron *et al.*<sup>22</sup>

results regarding the organization of the nitroaniline molecules in polar chains through three center hydrogen bonds. The apparent dissent can be explained because the bifurcated structure leaves the second amino hydrogen more available for interactions with neighboring chains favoring more effective three dimensional packing.

To help the analysis of the factors that govern the molecular organization, we further examined the hydrogen bonds scheme in MNA, *m*-NA and M5NA. Table 6 and Fig. 3 exhibit Panunto *et al.*<sup>1</sup> N—H···O hydrogen bond depiction for MNA and M5NA. These data show that in MNA, which displays a parallel chain arrangement, the interactions between chains are weaker than the interactions that induce chain formation. In M5NA, that displays an antiparallel chain arrangement, though the bond length of the intrachain interaction is of the same order as the one found in MNA, there are two interchain TC bonds. These bonds produce the centrosymmetric dimers and would cause interchain interactions stronger than the intrachain ones.

MNA m.p., 132°C, is higher than M5NA m.p., 106(1)°C. Neither the analysis of MNA and M5NA packing forces, given above, nor Dannenberg<sup>23</sup> findings, on optimal hydrogen bond interactions, explain the difference. The strong molecular conjugation in MNA allows one to assume the generation of cooperative effects, which would contribute with additional

stabilizing forces to the chains and might explain the m.p. difference. However, recent experimental and theoretical charge density studies of MNA<sup>24</sup> do not seem to support the hypothesis.

It is worth mentioning that the parameters which characterize *m*-NA's hydrogen bond were not included in the above discussion because our analysis, based in Ploug-Sorensen *et al.*<sup>6</sup> H's atoms positions retrieved from CSD,<sup>18</sup> indicates a hydrogen bond scheme different from Panunto *et al.* description.<sup>1</sup> In fact, the polar chains in *m*-NA originate from two TC hydrogen bonds, the donor atom of each being one H of the amino group and one of the H's *ortho* to it. Besides, interchain interactions are caused by short N—H···N contacts.

## Conclusions

The present study shows that the geometry of the molecules of M5NA in the crystalline state agrees with

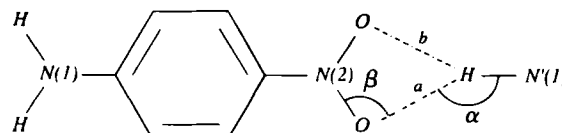


Fig. 3. Hydrogen bond's scheme and bond parameters used in Table 6.

Table 6. Geometry of the intermolecular contacts<sup>a</sup>

Compound	Space group	R (%)	Symmetry relation	N(H)···O(Å)	Length (Å)		Angle N—H···O	Angle N—O···H (°)
					a	b		
M5NA <sup>b</sup>	P2 <sub>1</sub> /n	4.3	Glide Inversion	3.151	2.34	2.79	147	154
				3.239	2.43	4.02	153	173
MNA <sup>c</sup>	Ia	4.0	Glide Glide	3.117	2.07	2.73	167	117
				3.234	2.23	4.22	152	220

<sup>a</sup> After Panunto *et al.*;<sup>1</sup> <sup>b</sup>This paper; <sup>c</sup>Howard *et al.*<sup>23</sup>

the degree of conjugation expected from the relative location of the substituents. The centrosymmetric packing is in accordance with the lack of nonlinear second order effects. The organization of the molecules in chains, in spite of the double bonded dimers formation, reinforce the Panunto *et al.*<sup>1</sup> assumption on the hydrogen bond driven polar chain structure formation in nitroanilines. However, it was found that the bifurcated character of those interactions proposed by the mentioned authors was not sustained in all the compounds.

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SUPPLEMENTARY MATERIAL. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5024. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: teched@chemcrs.cam.ac.uk).