

Fig. 2. Projection of the structure down the *b* axis (PITMOS). The hydrogen bonds are shown as dashed lines. The H atoms have been omitted.

There is an indication from this work that MMNO would not interact through its structuring N—O site with both the secondary hydroxyl groups OH(2) and OH(3) of the same glucose unit, merely on account of steric hindrance. Of the different ways of interaction of MMNO with cellulose, an interaction with hydroxyl groups belonging to two consecutive glucose residues of the cellulose backbone can be envisaged. Because of the overall  $2_1$  symmetry of the cellulose chain, this interaction would occur through hydrogen bonding between either the primary hydroxyl OH(6') and the secondary hydroxyl OH(2) or between the primary hydroxyl OH(6) and the secondary hydroxyl OH(3') of a contiguous glucose residue. This would result in a

stiffening of the cellulose chain. Examination of the possible modes of interaction between MMNO and cellulose is under study in our laboratory and will be reported later.

The authors thank Dr A. Péguy for growing the single crystals studied, and Professor D. Gagnaire for his continuous interest in this work. The data collection was performed within the 'Groupe Grenoblois de Diffractométrie'

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## Polarized Ethylenes: Structures of (1,3-Dimethyl-2-imidazolidinylidene)malononitrile and (1,3-Dimethyl-2-perhydropyrimidinylidene)malononitrile

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#### Abstract

Crystal structures of the title compounds, (I) and (II), have been determined by three-dimensional diffraction methods. Crystals of  $C_8H_{10}N_4$  (I) are monoclinic, space group  $P2_1/a$  with  $Z = 4$ ,  $M_r = 162$ ,  $a = 7.965$  (1),  $b = 16.232$  (2),  $c = 7.343$  (1) Å,  $\beta = 113.54$  (1)°,  $V = 890.7$  Å<sup>3</sup>,  $D_m = 1.218$ ,  $D_x = 1.208$  g cm<sup>-3</sup>,  $\mu(Cu K\alpha, \lambda = 1.5418 \text{ \AA}) = 6.47$  cm<sup>-1</sup>,  $F(000) = 344$ . The

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crystals of  $C_9H_{12}N_4$  (II) are orthorhombic, space group  $P2_1cn$ , with  $Z = 4$ ,  $M_r = 176$ ,  $a = 7.983$  (3),  $b = 8.075$  (2),  $c = 14.652$  (3) Å,  $V = 944.43$  Å<sup>3</sup>,  $D_m = 1.219$ ,  $D_x = 1.237$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha, \lambda = 0.7107 \text{ \AA}) = 0.868$  cm<sup>-1</sup>,  $F(000) = 376$ . Both structures were solved by direct methods and refined to  $R = 5.8\%$  for (I) and  $5.3\%$  for (II). The C—C double-bond distances are 1.407 (3) in (I) and 1.429 (6) Å in (II), appreciably longer than normal. The steric and push-pull effects

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result in rotation about the C=C bond, the rotation angles being  $20.2(3)$  in (I) and  $31.5(6)^\circ$  in (II).

### Introduction

A variety of substituted ethylenes have C=C bonds significantly longer than the bond in ethylene [ $1.336(2)$  Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965; Kuchitsu, 1966], e.g. trivinylborane,  $1.370(6)$  Å (Foord, Beagley, Reade & Steer, 1975), and *N,N',N'',N'''*-tetraphenyl-2,2'-bi(imidazolidinylidene),  $1.372(6)$  Å (Hitchcock, 1979). In olefins substituted with electron-releasing and electron-withdrawing groups in the vicinal positions such lengthening of the C=C bond is more pronounced with low barriers to rotation, e.g. dimethyl (dimethylaminomethylene)malonate,  $1.380(5)$  Å (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973);  $\alpha$ -(*p*-bromobenzoyl)- $\beta,\beta$ -bis(methylthio)acrylonitrile,  $1.369(7)$  Å, (*p*-bromobenzoyl)(1,3-dimethylimidazolidinylidene)acetonitrile,  $1.448(4)$  Å (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974). X-ray crystallographic results on a few other polarized ethylenes and related compounds have been reported (Shimanouchi, Ashida, Sasada & Kakudo, 1967; Ammon & Plastas, 1971; Hazell & Mukhopadhyay, 1980; Adhikesavalu & Venkatesan, 1981). In this paper we report X-ray results on (1,3-dimethyl-2-imidazolidinylidene)malononitrile (I) and (1,3-dimethyl-2-perhydropyrimidinylidene)malononitrile (II), samples of which were kindly provided by Professor J. Sandström, University of Lund, Sweden.

### Experimental

Single crystals of (I) were obtained from toluene by slow evaporation. The crystal used in the data collection had approximate dimensions  $0.6 \times 0.3 \times 0.2$  mm. Preliminary Weissenberg photographs indicated that the crystals are monoclinic, space group  $P2_1/a$ . Intensity data were collected on a CAD-4 diffractometer using Cu  $K\alpha$  ( $\lambda = 1.5418$  Å) radiation ( $\omega/2\theta$  mode) to a limit of  $\theta = 70^\circ$ , using a scan speed of  $1^\circ \text{ min}^{-1}$ . 1687 reflections were collected of which 1351 were significant,  $|F_o| \geq 3\sigma(|F_o|)$ . Single crystals of (II) were obtained from benzene by slow evaporation. The crystal used in the data collection had approximate dimensions  $0.7 \times 0.2 \times 0.2$  mm. Preliminary Weissenberg photographs indicated that the crystals are orthorhombic, space group  $P2_1cn$ . Intensity data were collected on a CAD-4 diffractometer using Mo  $K\alpha$  ( $\lambda = 0.7107$  Å) radiation to a limit of  $\theta = 23^\circ$ . 684 reflections were collected of which 538 were found to be significant,  $|F_o| \geq 2\sigma(|F_o|)$ .

### Structure solution and refinement

Structure (I) was solved using the direct-methods program *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Block-diagonal least-squares refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged at  $R = 7.5\%$ . At this stage nine strong low-angle reflections were corrected for secondary extinction using the relation proposed by Darwin (1922),  $g = 8 \times 10^{-5}$ . Full-matrix refinement gave a final  $R = 5.8\%$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/(a + bF + cF^2)$  with  $a = 2.0$ ,  $b = 1.0$  and  $c = 0.04$ .

Structure (II) was solved using the direct-methods program *SHELX 76* (Sheldrick, 1976). The best  $E$  map gave 12 out of 13 non-H atoms. The remaining atom was located from a difference map. Block-diagonal refinement of one scale factor, positional and anisotropic temperature factors (isotropic thermal parameters for H atoms, located from a difference map) gave a final  $R$  index of  $5.3\%$ . One H atom (H3) was not refined. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(|F_o|)$ . The block-diagonal least-squares program (Shiono, 1968) and full-matrix least-squares program (Gantzel, Sparks & Trueblood, 1966) were modified by B. S. Reddy and T. N. Bhat, respectively, to suit an IBM 360/44 computer.\*

### Discussion

Coordinates are recorded in Tables 1 and 2. Tables 3 and 4 give the bond lengths and angles, and some of the important torsion angles are given in Table 5. Figs. 1 and 2 give views and numbering of atoms for

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and some intramolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36409 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

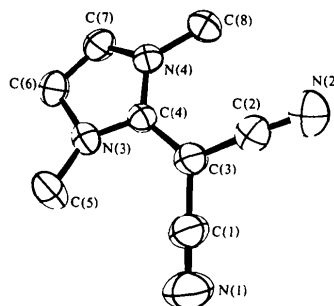


Fig. 1. Perspective view of the molecule (structure I).

Table 1. Fractional atomic coordinates ( $\times 10^4$ ,  $\times 10^3$  for H) and isotropic thermal parameters [ $B_{eq}$  for non-H atoms expressed as  $\frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ ;  $B$  for H atoms:  $T = \exp(-B \sin^2 \theta / \lambda^2)$ ] with e.s.d.'s in parentheses for structure (I)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
N(1)	5062 (4)	3272 (1)	6401 (4)	7.6 (0.1)
N(2)	6685 (4)	1004 (2)	9685 (3)	6.7 (0.1)
N(3)	3055 (2)	1610 (1)	2781 (2)	3.9 (0.1)
N(4)	2942 (2)	531 (1)	4563 (2)	3.6 (0.1)
C(1)	4975 (3)	2567 (1)	6355 (4)	4.9 (0.1)
C(2)	5818 (3)	1301 (1)	8178 (3)	4.5 (0.1)
C(3)	4831 (3)	1697 (1)	6341 (3)	3.7 (0.1)
C(4)	3651 (2)	1282 (1)	4625 (3)	3.1 (0.1)
C(5)	4074 (4)	2207 (2)	2142 (5)	5.6 (0.1)
C(6)	1931 (4)	1003 (2)	1332 (3)	5.1 (0.1)
C(7)	1482 (4)	389 (2)	2588 (4)	4.8 (0.1)
C(8)	2848 (4)	86 (2)	6244 (4)	4.6 (0.1)

Bonded to	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1) C(5)	551 (6)	215 (2)	308 (7)	6.5 (1.0)
H(2) C(5)	333 (7)	229 (3)	40 (8)	8.3 (1.2)
H(3) C(5)	443 (10)	284 (5)	287 (11)	14.0 (2.1)
H(4) C(6)	256 (4)	75 (2)	56 (5)	3.7 (0.6)
H(5) C(6)	86 (5)	131 (2)	33 (5)	4.7 (0.7)
H(6) C(7)	148 (4)	-21 (2)	209 (5)	4.0 (0.7)
H(7) C(7)	36 (4)	52 (2)	267 (4)	2.7 (0.5)
H(8) C(8)	263 (6)	41 (3)	728 (7)	6.8 (1.0)
H(9) C(8)	225 (6)	-44 (2)	578 (6)	5.7 (0.9)
H(10) C(8)	405 (6)	-4 (2)	729 (6)	5.3 (0.8)

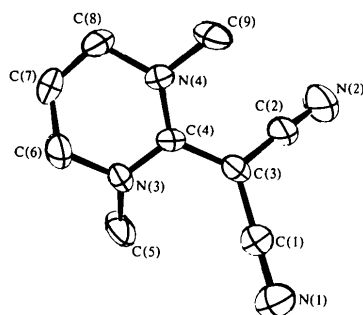


Fig. 2. Perspective view of the molecule (structure II).

molecules (I) and (II). The C=C bonds in (I) and (II) are 1.407 (3) and 1.429 (6) Å, both substantially longer than the value for the C=C bond in ethylene. Moreover the N(3)-C(4) and N(4)-C(4) distances in (I) and (II) [1.335 (5)-1.352 (2) Å] are significantly shorter than the corresponding N-C distance of 1.395 (3) and 1.403 (3) Å in *N,N',N'',N'''*-tetraphenyl-2,2'-bi(imidazolidinylidene) (Hitchcock, 1979), while on the acceptor side the C(3)-C(1) and C(3)-C(2) bonds in (I) and (II) [1.395 (7)-1.418 (3) Å] are distinctly shorter than the corresponding C-CN distance of 1.437 (2) Å in ethylene-tetracarbonitrile (Little, Pautler & Coppens, 1971).

Both (I) and (II) contain the unit (A) and these bond-length results demonstrate that forms such as (B) must contribute to the electronic structure.

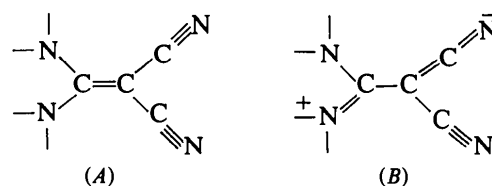


Table 2. Fractional atomic coordinates ( $\times 10^4$ ,  $\times 10^3$  for H) and isotropic thermal parameters [ $B_{eq}$  for non-H atoms expressed as  $\frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ ;  $B$  for H atoms:  $T = \exp(-B \sin^2 \theta / \lambda^2)$ ] with e.s.d.'s in parentheses for structure (II)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
N(1)	9790	8903 (6)	5243 (4)	5.8 (0.2)
N(2)	7455 (9)	4566 (6)	6396 (3)	6.0 (0.2)
N(3)	7837 (7)	6607 (4)	3367 (2)	3.4 (0.1)
N(4)	8103 (7)	3911 (4)	3861 (3)	3.5 (0.1)
C(1)	9189 (9)	7659 (6)	5103 (3)	3.9 (0.1)
C(2)	7912 (10)	5238 (6)	5732 (3)	4.1 (0.2)
C(3)	8387 (8)	6123 (5)	4957 (3)	3.1 (0.1)
C(4)	8063 (8)	5526 (5)	4056 (3)	2.9 (0.1)
C(5)	6995 (10)	8218 (7)	3509 (4)	4.7 (0.2)
C(6)	7860 (11)	5953 (6)	2434 (3)	4.8 (0.2)
C(7)	6760 (10)	4473 (8)	2391 (4)	5.2 (0.2)
C(8)	7392 (10)	3175 (7)	3030 (4)	4.9 (0.2)
C(9)	8941 (9)	2685 (6)	4457 (4)	4.5 (0.2)

Bonded to	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1) C(5)	696 (7)	846 (6)	420 (3)	3.4 (1.1)
H(2) C(5)	581 (10)	847 (8)	319 (4)	6.5 (1.7)
H(3)* C(5)	800	900	333	6.0
H(4) C(6)	736 (6)	687 (5)	202 (3)	2.3 (0.9)
H(5) C(6)	907 (11)	555 (8)	235 (5)	7.8 (1.8)
H(6) C(7)	552 (10)	456 (8)	274 (4)	6.5 (1.6)
H(7) C(7)	688 (7)	391 (6)	183 (3)	3.4 (1.1)
H(8) C(8)	628 (8)	261 (7)	319 (4)	5.5 (1.5)
H(9) C(8)	858 (8)	248 (6)	280 (4)	4.4 (1.2)
H(10) C(9)	1004 (10)	319 (8)	485 (5)	6.7 (1.7)
H(11) C(9)	985 (11)	214 (10)	420 (5)	8.4 (2.1)
H(12) C(9)	780 (12)	204 (8)	477 (5)	7.9 (1.9)

\* Not refined.

Table 3. Bond distances (Å) with e.s.d.'s in parentheses

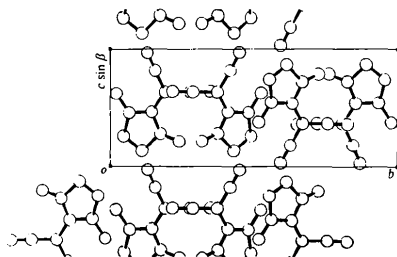
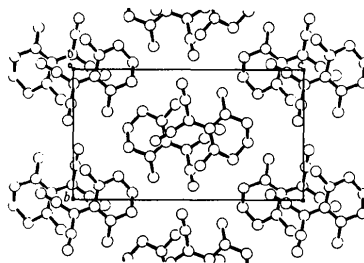
	(I)	(II)
N(1)-C(1)	1.145 (3)	1.132 (7)
N(2)-C(2)	1.151 (3)	1.173 (7)
C(1)-C(3)	1.418 (3)	1.412 (7)
C(2)-C(3)	1.415 (3)	1.395 (7)
C(3)-C(4)	1.407 (3)	1.429 (6)
C(4)-N(3)	1.352 (2)	1.347 (5)
C(4)-N(4)	1.337 (2)	1.335 (5)
N(3)-C(5)	1.458 (4)	1.479 (7)
N(3)-C(6)	1.464 (3)	1.465 (6)
C(6)-C(7)	1.495 (4)	1.485 (10)
C(7)-C(8)	-	1.493 (9)
C(7)-N(4)	1.470 (3)	-
C(8)-N(4)	1.457 (3)	1.469 (7)
C(9)-N(4)	-	1.480 (7)

Table 4. Bond angles (°) involving non-H atoms with e.s.d.'s in parentheses

	(I)	(II)
C(3)–C(1)–N(1)	177.9 (3)	177.5 (6)
C(3)–C(2)–N(2)	176.9 (3)	176.3 (6)
C(1)–C(3)–C(2)	115.7 (2)	116.7 (5)
C(1)–C(3)–C(4)	120.5 (2)	121.2 (5)
C(2)–C(3)–C(4)	123.6 (2)	122.0 (5)
C(3)–C(4)–N(3)	123.4 (2)	119.8 (5)
C(3)–C(4)–N(4)	126.1 (2)	121.5 (5)
C(4)–N(3)–C(5)	124.5 (2)	121.7 (4)
C(4)–N(3)–C(6)	109.3 (2)	117.6 (4)
C(4)–N(4)–C(9)	–	122.5 (5)
C(4)–N(4)–C(8)	125.9 (2)	124.3 (5)
C(4)–N(4)–C(7)	109.5 (2)	–
C(5)–N(3)–C(6)	118.1 (2)	117.0 (5)
N(3)–C(6)–C(7)	103.1 (2)	108.8 (5)
C(6)–C(7)–C(8)	–	109.7 (5)
C(6)–C(7)–N(4)	102.4 (2)	–
C(7)–C(8)–N(4)	–	111.5 (5)
C(7)–N(4)–C(8)	118.1 (2)	–
C(8)–N(4)–C(9)	–	113.1 (4)
N(4)–C(4)–N(3)	110.5 (2)	118.4 (5)

Table 5. Torsion angles (°) with e.s.d.'s in parentheses

(I)	
C(1)–C(3)–C(4)–N(3)	21.5 (3)
C(2)–C(3)–C(4)–N(3)	–163.8 (2)
C(1)–C(3)–C(4)–N(4)	–157.4 (2)
C(2)–C(3)–C(4)–N(4)	17.4 (3)
C(4)–N(3)–C(6)–C(7)	16.6 (2)
N(3)–C(6)–C(7)–N(4)	–21.6 (2)
C(6)–C(7)–N(4)–C(4)	20.9 (2)
C(7)–N(4)–C(4)–N(3)	–11.3 (2)
N(4)–C(4)–N(3)–C(6)	–3.8 (2)
(II)	
C(1)–C(3)–C(4)–N(3)	–28.3 (8)
C(2)–C(3)–C(4)–N(3)	150.9 (5)
C(1)–C(3)–C(4)–N(4)	146.6 (5)
C(2)–C(3)–C(4)–N(4)	–34.3 (8)
C(4)–N(3)–C(6)–C(7)	48.1 (7)
N(3)–C(6)–C(7)–C(8)	–60.7 (7)
C(6)–C(7)–C(8)–N(4)	35.4 (7)
C(7)–C(8)–N(4)–C(4)	5.2 (8)
C(8)–N(4)–C(4)–N(3)	–20.9 (8)
N(4)–C(4)–N(3)–C(6)	–7.5 (7)

Fig. 3. Packing of the molecules viewed down *a* for structure (I).Fig. 4. Packing of the molecules viewed down *a* for structure (II).

The rotation about the C=C bond as measured by the angle between the planes through the atoms N(3), N(4) and C(4) and C(1), C(2) and C(3) is 20.2 (3)° in (I) and 31.5 (6)° in (II). Assuming planar geometry for both the molecules, the calculated intramolecular distances show some close contacts. This steric strain results in twist about the C=C bond leading to a more stable conformation and the higher twist angle in (II) is due to the greater steric effect in that molecule. The longer C=C bond distances in (II) suggests that the perhydropyrimidine ring is a better electron-releasing group compared to the imidazolidine ring. The dipole moment values of  $26.49 \times 10^{-30}$  and  $26.79 \times 10^{-30}$  Cm for (I) and (II) (Ericsson, Marnung, Sandström & Wennerbeck, 1975) are qualitatively consistent with the observed difference in C=C bond lengths. The imidazolidine ring has an envelope conformation with C(7) out of plane. The packing of molecules in the unit cell is shown in Figs. 3 and 4.

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## The Structure of the 1:1 Molecular Complex of Pyrene and Dicyanomethylenecroconate\*

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### Abstract

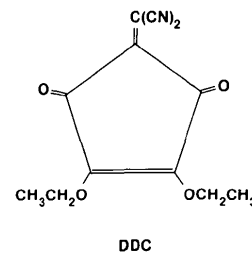
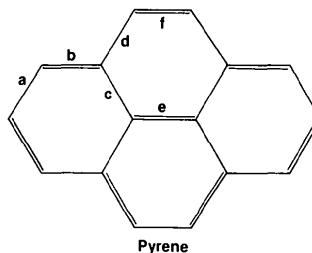
$C_{16}H_{10} \cdot C_{12}H_{10}N_2O_4$  is triclinic,  $P\bar{1}$ , with  $a = 10.085$  (3),  $b = 10.646$  (3),  $c = 11.037$  (3) Å,  $\alpha = 98.73$  (2),  $\beta = 92.61$  (2),  $\gamma = 107.36$  (2)°,  $Z = 2$ ,  $D_x = 1.339$ ,  $D_m = 1.35$  g cm<sup>-3</sup>,  $\mu$ (Cu  $K\alpha$ ) = 6.96 cm<sup>-1</sup>. Final  $R = 0.048$  for 2767 observed reflections. The compound, which is a 1:1 molecular complex of pyrene and dicyanomethylenecroconate, is formed upon evaporation of a solution containing equimolar amounts of the two substances. The structure of this charge-transfer complex consists of stacks of alternating donor and acceptor molecules.

### Introduction

Treatment of diethylcroconate in *N,N*-dimethylformamide with malononitrile produces golden plates of 2-(3,4-diethoxy-2,5-dioxo-3-cyclopenten-1-ylidene)-malononitrile (DDC) in 85% yield (Fatiadi, 1978*a*). DDC is an electron acceptor; for example, with polycyclic aromatic hydrocarbons such as pyrene, benz[*a*]pyrene, or anthracene it forms deeply colored charge-transfer complexes. This paper describes the crystal and molecular structure of a 1:1 molecular complex (hereafter referred to as P-DDC) formed from pyrene and DDC.

\* Dicyanomethylenecroconate is 2-(3,4-diethoxy-2,5-dioxo-3-cyclopenten-1-ylidene)malononitrile.

† From a dissertation submitted to the Graduate School, University of Maryland, in partial fulfillment of the requirements for a PhD degree in chemistry.



Ruby-red crystals of P-DDC (m.p. 441–443 K) were prepared by slow evaporation to dryness of a dichloromethane solution of an equimolar amount of pyrene and DDC (Fatiadi, 1978*a*). An elemental analysis of the product gave the following results. Calculated (found) for  $C_{28}H_{20}N_2O_4$ : C 74.99 (75.15), H 4.49 (4.68), N 6.25 (6.38)%. The mass spectrum showed only two peaks, one at  $m/e$  202 (pyrene) and one at  $m/e$  246 (DDC). The ultraviolet spectrum, recorded in dichloromethane, showed bands at  $\lambda_{max}$  of 439*sh* ( $\epsilon = 10\,000$ ), 413 ( $\epsilon = 12\,700$ ), 338.7 ( $\epsilon = 54\,000$ ), 322.4 ( $\epsilon = 32\,000$ ), 307 ( $\epsilon = 16\,300$ ), and 295 nm ( $\epsilon = 8200$ ). The infrared spectrum (KBr) showed the following maxima: 2220*w* (C≡N), 1660*s* (C=O, C=C), 1640*w*, 1600*w*, 1552*s*, 1470*m*, 1429*m*, 1390*s*, 1360*m*, 1330*s*, 1235*m*, 1176*m*, 1136*s*, 1108*w*, 1075*w*, 1010*s*, 901*m*, 862*m*, 847*s*, 826*w*, 785*m*, 763*m*, 754*s*, 714*s* cm<sup>-1</sup>.

Data were collected on a crystal of dimensions 0.20 × 0.20 × 0.05 mm using an automated four-circle diffractometer with graphite-monochromated Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å. Cell dimensions were determined by a least-squares refinement of the setting angles of 15 reflections with  $2\theta$  values ranging between