The Action of Amines on Citraconic Anhydride. X-Ray Crystal Structure of (Z)-2-Methyl-3-pyrrolidinocarbonylpropenoic Acid

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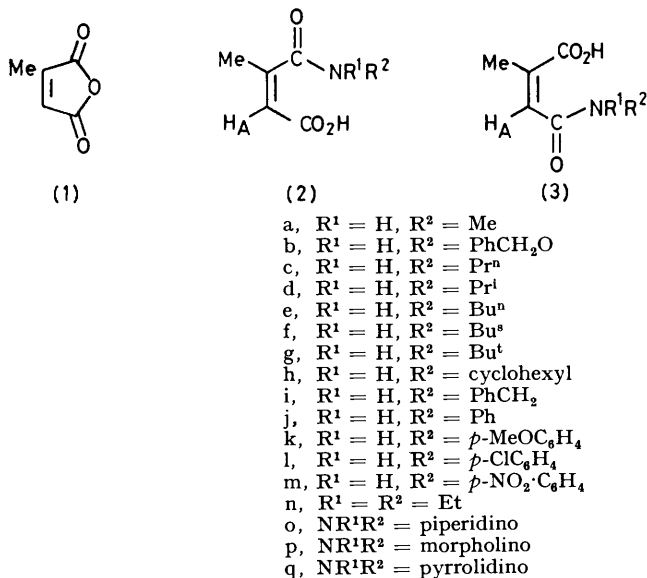John Aupers and Peter F. Lindley,* Department of Crystallography, Birkbeck College, London WC1E 7HX

The reaction of citraconic anydride with 15 primary and secondary amines gave mixtures of isomeric citraconamic acids (2) and (3), in which the former predominated. The more abundant isomers rearranged to the thermodynamically stable N-substituted (Z)-2-methyl-3-carbamoylpropenoic acids (3) on warming. The structure of the pyrrolidide (3q) was confirmed by X-ray analysis. An unsuccessful attempt to convert the pyrrolidide into 4-methyl-6-pyrrolidino-1,3-oxazin-2-one (7) is described.

IN the course of our work on the synthesis of 1,3-oxazin-2-ones, which starts with substituted maleic anhydrides,[1] we became interested in the structures of citraconamic acids. There are conflicting reports on the reactions of amines with citraconic anhydride. In 1959 Russian authors [2] treated the anhydride with a series of primary amines and in each case obtained a single amic acid, which they stated had structure (2; $R^1 = H$, $R^2 =$ alkyl). No reason for this assignment was given. The following year, Mehta et al.[3] described the reactions of several primary aliphatic and aromatic amines and pyrrolidine with citraconic anhydride and claimed that primary amines gave mixtures of the two possible amic acids (2) and (3), which were separated by fractional

(1)

(2)

(3)

a, $R^1 = H$, $R^2 = Me$
b, $R^1 = H$, $R^2 = PhCH_2O$
c, $R^1 = H$, $R^2 = Pr^n$
d, $R^1 = H$, $R^2 = Pr^i$
e, $R^1 = H$, $R^2 = Bu^n$
f, $R^1 = H$, $R^2 = Bu^s$
g, $R^1 = H$, $R^2 = Bu^t$
h, $R^1 = H$, $R^2 = $ cyclohexyl
i, $R^1 = H$, $R^2 = PhCH_2$
j, $R^1 = H$, $R^2 = Ph$
k, $R^1 = H$, $R^2 = p\text{-MeOC}_6H_4$
l, $R^1 = H$, $R^2 = p\text{-ClC}_6H_4$
m, $R^1 = H$, $R^2 = p\text{-NO}_2\cdot C_6H_4$
n, $R^1 = R^2 = Et$
o, $NR^1R^2 = $ piperidino
p, $NR^1R^2 = $ morpholino
q, $NR^1R^2 = $ pyrrolidino

crystallisation, whereas pyrrolidine afforded a single isomer. No attempt was made to determine the structures of the products. Kirby and Lancaster [4] were unable to repeat this work. Although in the synthesis of N-n-propylcitraconamic acid various fractions having different melting points were obtained, they all proved to be homogeneous and identical by t.l.c. Determined efforts to separate the supposedly isomeric N-methyl-citraconamic acids by t.l.c., paper chromatography, electrophoresis, ion-exchange, and column chromato-

graphy were unsuccessful. An alternative synthesis of the N-methyl compound by hydrolysis of N-methyl-citraconimide gave an identical product. It was concluded that the action of methylamine on citraconic anhydride gave a single isomer with the orientation (3a). It was stated that the structure had been confirmed by X-ray crystallography. More recently, Ollis and his colleagues [5] found that citraconic anhydride reacted with O-benzylhydroxylamine to give a single amic acid, which was shown to be (3b) by chemical degradation. We have now found that the action of amines on citraconic anhydride results in mixtures of citraconamic acids and that one isomer rearranges to the other so readily that only one can be isolated.

Ethereal solutions of a number of primary and secondary amines were mixed with equimolecular amounts of citraconic anhydride at slightly below room temperature, the solvent was removed in vacuo without heating, and the ^{1}H n.m.r. spectra of solutions of the residues in dimethyl sulphoxide were determined. In each of the 15 cases studied, the spectra exhibited two sets of signals due to olefinic protons and C-methyl groups, which we attribute to the presence of the isomeric citraconamic acids (2) and (3). The former signals appeared as quartets and the latter as doublets, with allylic coupling constants of 1.4—1.6 Hz. The proportions of the isomers were estimated from the integrated signals due to the olefinic protons; their chemical shifts and ratios are listed in Table 1. It is seen that in nearly every case the amic acid, whose olefinic proton H_A resonates at higher field, preponderates. The isomers having H_A and H_B are assigned structures (2) and (3), respectively, on the basis of the chemical shifts of the olefinic protons. Examination of the signals of olefinic protons in over a thousand compounds led Pascual, Meier, and Simon [6] to formulate a set of 'additivity rules'. Application of these rules to the citraconamic acids leads to the conclusion that the olefinic protons of compounds (2) should be more shielded than those of the isomers (3). The structure of the pyrrolidide (3q) was confirmed by X-ray analysis (see later).

An attempt was made to separate the isomeric pyrrolidine derivatives (2q) and (3q). The crude mixture of isomers was crystallised from hot methanol, giving the crystalline acid of m.p. 110 °C, obtained by the

TABLE 1

Proportions of citraconamic acids (2) and (3) in the reaction mixtures obtained from amines and citraconic anhydride

|	Amine	δ[(CD₃)₂SO]		Ratio (2) : (3)
		H_A	H_B	
c,	n-Propylamine	5.83	5.98	65 : 35
d,	Isopropylamine	5.82	6.01	50 : 50
e,	n-Butylamine	5.77	6.18	50 : 50
f,	s-Butylamine	5.65	5.95	60 : 40
g,	t-Butylamine	5.65	6.15	60 : 40
h,	Cyclohexylamine	5.68	6.27	60 : 40
i,	Benzylamine	5.89	6.01	60 : 40
j,	Aniline	5.83	6.18	60 : 40
k,	p-Anisidine	5.81	6.16	65 : 35
l,	p-Chloroaniline	5.85	6.15	65 : 35
m,	p-Nitroaniline	5.93	6.20	57 : 43
n,	Diethylamine	5.79	6.28	70 : 30
o,	Piperidine	5.79	6.16	78 : 22
p,	Morpholine	5.78	6.23	75 : 25
q,	Pyrrolidine	5.78	6.23	70 : 30

American workers.[3] The filtrate on evaporation gave more of the same compound, whose n.m.r. spectrum showed it to be (3q). Hence the major product had rearranged to the minor isomer during the recrystallisation. Similar results were obtained with the other citraconamic acids: in each case the isomer with the less shielded proton was obtained in 80—95% yield after recrystallisation from a hot solvent. Examination of the n.m.r. spectra of the mother liquors showed the absence of the labile amic acid. The physical properties and analyses of the isolated citraconamic acids (3) are collected in Table 2.

The isomerisation of the citraconamic acids (2)→(3) was found to be temperature- and solvent-dependent. Thus, the ¹H n.m.r. spectrum of a freshly prepared solution in dimethyl sulphoxide of the crude product mixture of the reaction of aniline with citraconic anhydride indicated that it contained 60% of the anilic acid (2j) and 40% of (3j); after 110 min at 35 °C the content of (2j) had fallen to 54%. After 110 min at 65 °C the

decrease was to 45%, and to 33% after 110 min at 95 °C. A much faster isomerisation occurred in deuteriochloroform; in trifluoroacetic acid the rearrangement was so rapid that the presence of the labile amic acids (2) could not be detected.

We conclude that the reaction of amines with citraconic anhydride is reversible; the amic acids (2) are the products of kinetic control, which rearrange to the more stable isomers (3). Previous failures to detect or isolate isomeric citraconamic acids are therefore not surprising.
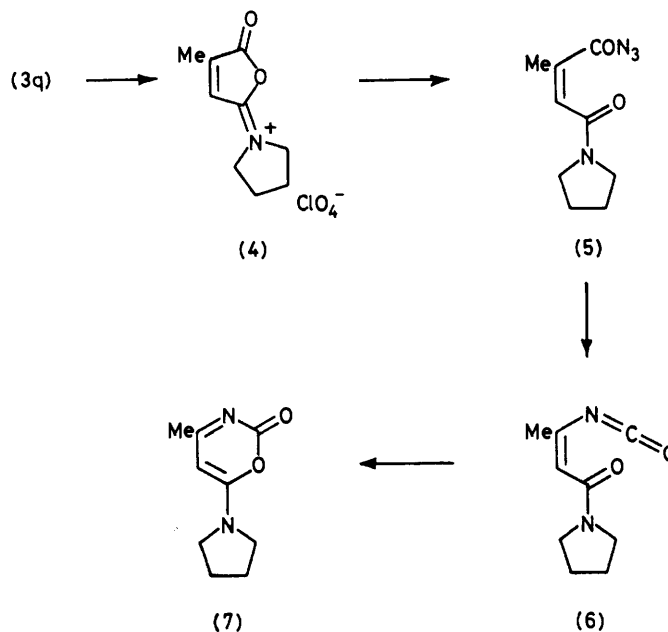
The pyrrolidide (3q) was converted into the isoimidium salt (4) by the action of acetic anhydride and perchloric acid. Treatment of the salt with sodium azide gave the crystalline acyl azide (5), which was decomposed in boiling toluene. The i.r. spectrum of the solution,

TABLE 2

N-Substituted (Z)-2-methyl-3-carbamoylpropenoic acids (3)

		I.r. (cm⁻¹)		δ [(CD₃)₂SO]		Analyses (%)						
		CO	CO			Found				Required		
Compound	M.p. (°C)	Acid	Amide	H_B	Me	C	H	N	Formula	C	H	N
(3c)	132—133 a,b	1 695	1 637	6.00	2.10	56.2	7.7	7.9	C₈H₁₃NO₃	56.15	7.7	8.2
(3d)	129—130 a,c	1 700	1 638	6.17	1.96	56.5	7.4	7.9	C₈H₁₃NO₃	56.15	7.7	8.2
(3e)	121—122 a,d	1 702	1 644	6.18	1.95	58.2	8.4	7.6	C₉H₁₅NO₃	58.4	8.2	7.6
(3f)	118—119 a	1 705	1 640	6.65	2.10	58.1	8.4	7.3	C₉H₁₅NO₃	58.4	8.2	7.6
(3g)	127—128 e	1 695	1 630	6.15	1.93	58.5	8.4	7.6	C₉H₁₅NO₃	58.4	8.2	7.6
(3h)	144—145 a,f	1 695	1 635	6.25	1.95	62.8	8.3	6.3	C₁₁H₁₇NO₃	62.5	8.1	6.6
(3i)	124—126 e,g	1 695	1 630	6.13	1.96	65.7	6.0	6.4	C₁₂H₁₄NO₃	65.5	5.9	6.3
(3j)	170—172 h,i	1 703	1 630	6.18	2.02	64.2	5.4	6.8	C₁₁H₁₁NO₃	64.4	5.4	6.8
(3k)	175—176 h	1 690	1 625	6.16	1.99	61.0	5.3	5.7	C₁₂H₁₃NO₄	61.3	5.6	6.0
(3l)	180—181 h	1 705	1 628	6.05	2.05	55.3	4.2	5.7	C₁₁H₁₁ClNO₃	55.1	4.2	5.8
(3m)	168—169 h	1 700	1 628	6.20	2.08	52.8	4.0	11.1	C₁₁H₁₀N₂O₅	52.8	4.0	11.2
(3n)	96—97 a	1 710	1 590	6.28	2.08	58.1	8.4	7.5	C₉H₁₅NO₃	58.4	8.2	7.6
(3o)	101—102 a	1 705	1 580	6.15	1.85	60.6	7.9	7.1	C₁₀H₁₅NO₃	60.8	7.7	7.1
(3p)	120—121 k	1 710	1 590	6.25	1.92	54.1	6.8	7.0	C₉H₁₃NO₄	54.3	6.6	7.05
(3q)	108—109 a,j	1 705	1 590	6.22	1.80	59.0	7.4	7.4	C₉H₁₃NO₃	59.0	7.15	7.65

a From ethyl acetate. b Lit.,[4] m.p. 129.5—130.5 °C and lit.,[3] m.p.s 122 and 140 °C for the 'two isomers'. c Lit.,[2] m.p. 118.5—119 °C. d Lit.,[2] m.p. 113.5 °C. e From benzene. f Lit.,[2] m.p. 134.5—135 °C. g Lit.,[3] m.p.s 132 and 142 °C for the 'Two isomers'. h From ethanol. i Lit.,[3] m.p.s 172 and 184 °C for the 'two isomers'. j Lit.,[3] m.p. 110 °C. k From benzene–light petroleum.

determined at intervals, indicated that the decomposition took *ca.* 1 h. No bands attributable to the Curtius rearrangement product, the isocyanate (6), were observed. The absorptions due to the azide were replaced by a strong sharp band at 1 760 cm^{-1}, which soon disappeared. At the same time the solution became red and then dark-brown. T.l.c. of the mixture indicated the presence of at least eight products. We attribute the band at 1 760 cm^{-1} to the oxazinone (7), formed by rapid electrocyclisation of the transient

is appreciably longer than the double bond between C(1) and O(2) in the carboxylic acid moiety, 1.208(5) Å. The C(5)–N(5) distance, 1.324(5) Å, compares with the value of 1.29 Å for a C–N double bond indicating a considerable amount of double bond character in this linkage and in conjunction with this the geometry at N(5) is planar. The opening out of the C(5)–N(1)–C(9) angle to 128.2(3)° compared with that of 120.8(3)° for C(5)–N(1)–C(6) is due to non-bonded repulsions between O(3) and the methylene hydrogen atoms at C(9).
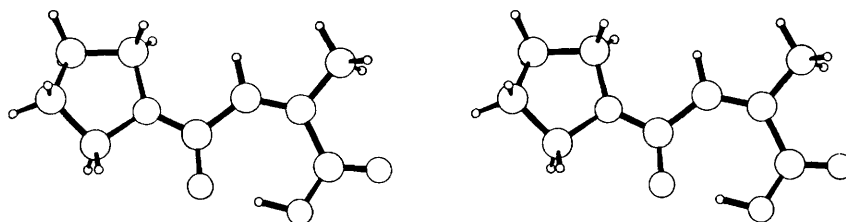

FIGURE 1 A stereo-drawing of the molecule (3q) viewed along the unit cell *b* axis

isocyanate (6).[1] The azide therefore had the configuration shown and no isomerisation occurred during its formation.[1] The oxazinone is probably too unstable to survive the conditions required for the Curtius rearrangement.

Description of Structure (3q).—Figure 1 is a stereo-drawing of the molecule viewed along the unit cell *b* axis and clearly shows the methyl group at C(3) and the intramolecular hydrogen bond between the hydroxy-group at C(1) and the oxygen atom O(3) at C(5). Figure 2 is a
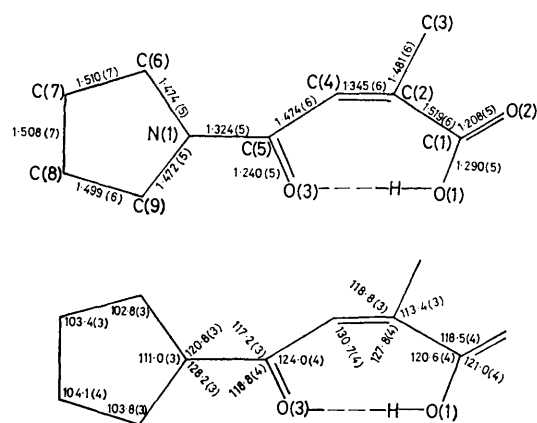

FIGURE 2 A schematic drawing of the molecule (3q) showing the intramolecular bond lengths and angles and their associated standard deviations

schematic drawing of the molecule showing the intramolecular bond lengths and angles together with their estimated standard deviations. Further details of the molecular geometry are listed in Table 3.

The molecular skeleton is approximately planar and lies parallel to (010). The planarity of the 3-methyl-1-oxo-but-2-enoic acid moiety is maintained by an intramolecular hydrogen bond; the O(1)–O(3) separation is 2.44(1) Å. In accordance with the presence of this hydrogen bond the C(5)–O(3) bond distance, 1.240(5) Å,

TABLE 3

Positional parameters for non-hydrogen atoms in (3q) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U. 10^4†
O(1)	−0.231 9(5)	0.257 8(5)	1.059 7(3)	63
O(2)	−0.075 8(5)	0.237 0(5)	1.259 4(3)	68
O(3)	−0.135 3(5)	0.271 7(4)	0.856 2(3)	57
N(1)	0.146 5(5)	0.252 1(4)	0.781 1(3)	42
C(1)	−0.064 8(7)	0.246 5(5)	1.150 1(4)	45
C(2)	0.151 0(6)	0.246 7(5)	1.121 3(4)	45
C(3)	0.326 6(7)	0.242 7(7)	1.236 6(4)	57
C(4)	0.195 9(6)	0.248 6(5)	1.006 7(4)	41
C(5)	0.057 2(6)	0.257 3(5)	0.878 1(4)	41
C(6)	0.021 5(7)	0.268 2(7)	0.649 7(4)	54
C(7)	0.191 1(9)	0.314 2(8)	0.577 7(4)	70
C(8)	0.366 9(8)	0.202 5(9)	0.646 3(5)	76
C(9)	0.368 3(6)	0.229 6(7)	0.783 9(4)	56

† Spherically averaged U_{ij}. 10^3 (Å^2). Expression for U_{iso}. is exp $(-8\pi^2 . U_{iso}.\sin^2\theta/\lambda^2)$.

The conformation of the pyrrolidine ring is closer to the half-chair rather than the envelope form; the pseudorotational phase parameters,[7] taking the torsion angle C(6)–C(7)–C(8)–C(9) as ϕ_0, are $\Delta = 11.7°$ ($\Delta = 0$ and 36° for idealised half-chair and envelope conformations

TABLE 4

Molecular geometry

(*a*) Least-squares plane defined by atomic positions and in parentheses the distances of atoms from the planes (Å). *X*, *Y* and *Z* refer to orthogonal axes obtained by the transformation;

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a\sin\beta\sin\gamma & 0 & 0 \\ -a\sin\beta\cos\gamma & b.\sin\alpha & 0 \\ a\cos\beta & b.\cos\alpha & c \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Plane (i): All non-hydrogen atoms

0.2116X + 0.9769Y + 0.0300Z = 2.0714

[O(1) −0.07, O(2) −0.07, O(3) 0.00, N(1) −0.03, C(1) −0.04, C(2) 0.05, C(3) 0.14, C(4) 0.05, C(5) 0.00, C(6) −0.02, C(7) 0.34, C(8) −0.30, C(9) −0.08]

(*b*) Torsion angles (°) for the pyrrolidine ring.

N(1)–C(6)–C(7)–C(8)	33.3
C(6)–C(7)–C(8)–C(9)	−39.1
C(7)–C(8)–C(9)–N(1)	28.9
C(8)–C(9)–N(1)–C(6)	−8.0
C(9)–N(1)–C(6)–C(7)	−15.9

respectively) and $\phi_m = -39.9°$. There are no inter-molecular distances that are significantly less than the sum of the corresponding van der Waals' radii.

EXPERIMENTAL

For general remarks, see ref. 1.

The Action of Amines on Citraconic Anhydride.—A solution of an amine (1 mmol) in anhydrous ether (10 ml) was added dropwise to a cooled, stirred solution of citraconic anhydride (0.112 g, 1 mol equiv.) in ether (10 ml) at such a rate that the temperature remained at 10—15 °C. The mixture was stirred for a further 30 min, during which time the products precipitated in most cases. The ether was removed under reduced pressure at room temperature; the solid or semi-solid residue was dissolved in deuteriated dimethyl sulphoxide and the ^{1}H n.m.r. spectrum of the solution was determined at 90 MHz (see Table 1). The experiments were repeated on a 20 mmol scale. The crude products were repeatedly recrystallised, giving the stable N-substituted (Z)-2-methyl-3-carbamolypropenoic acids (3) in 80—95% yields (see Table 2).

An Attempt to prepare 4-Methyl-6-pyrrolidino-2H-1,3-oxazin-2-one (7).—Perchloric acid (3 ml) was added dropwise to a suspension of the pyrrolidide (3q) (3.66 g, 20 mmol) in ice-cold acetic anhydride (20 ml). The resulting solution was treated with ether to incipient cloudiness, whereupon 2,5-*dihydro-3-methyl-5-pyrrolidiniofuran-2-one* *perchlorate* (4) (4.48 g, 83%) crystallised. It had m.p. 173—175 °C (decomp.), $v_{max.}$ 1 840, 1 700, and 1 080 cm^{-1}; δ(CDCl$_3$) 7.58 (d, J 1.5 Hz, =CH), 4.3—4.0 (m, 4 H) and 2.4—2.1 (m, 4 H) (pyrrolidino), and 2.32 (d, J 1.5 Hz, Me) (Found: C, 40.6; H, 4.6; Cl, 13.6; N, 5.3. C$_9$H$_{12}$ClNO$_6$ requires C, 40.7; H, 4.6; Cl, 13.4; N, 5.3%). The salt (2.65 g, 10 mmol) was added to a stirred solution of sodium azide (1.3 g, 2 mol equiv.) in a mixture of water (5 ml) and acetone (10 ml). The acetone was removed *in vacuo* at room temperature and the resulting (Z)-2-methyl-3-pyrrolidinocarbonyl-propenoyl azide (5) (1.82 g, 88%) was collected. It had m.p. 90—91 °C (decomp.), $v_{max.}$ 2 168w, 2 140, 1 715, and 1 638 cm^{-1}; δ 4.93 (d, J 1.6 Hz, =CH), 3.4 (m, 4 H) and 2.1—1.7 (m, 4 H) (pyrrolidino), and 2.3 (d, J 1.6 Hz, Me). A solution of the azide (1.04 g) in benzene (20 ml) was boiled under reflux; samples were withdrawn at intervals and their i.r. spectra determined. The azide absorptions gradually diminished and a strong band at 1 760 cm^{-1} appeared. The solution darkened before all the azide had reacted and the band at 1 760 cm^{-1} disappeared. The resulting dark-brown solution showed no absorption above 1 630 cm^{-1} in the carbonyl region. T.l.c. indicated the presence of at least 8 components. The azide required one hour's heating for complete decomposition.

Crystal Data: C$_9$H$_{13}$NO$_3$, $M = 183.2$, triclinic, $a = 6.543(1)$, $b = 6.796(1)$, $c = 10.847(1)$ Å, $\alpha = 90.74(1)$, $\beta = 104.11(1)$, $\gamma = 97.35(1)°$, $U = 463.4$ Å^3, $Z = 2$, $D_c = 1.31$ g cm^{-3}, $F(000) = 196$. Space group $P\bar{1}$ (No. 2), μ(Cu-K_α) = 8.3 cm^{-1}.

The compound forms colourless prismatic crystals elongated along the b axis. Preliminary unit-cell dimensions and space-group information were obtained from precession photographs. All crystals examined showed appreciable mosaic spread in the X-ray beam but attempts

to minimise this feature by recrystallisation were unsuccessful. Crystals of related compounds with different substituents at C(5) (*e.g.* morpholino) were also studied but generally showed an even greater mosaic spread than the above compound and in some cases showed signs of gross disorder.

Intensity data were collected on a Hilger and Watts Y290 four-circle automated diffractometer using Ni filtered copper radiation and the $\omega/2\theta$ step scanning technique. The scan width was chosen to be 1.28° to allow for the mosaic spread of the crystal and the step size used was 0.02° with a count time of 1 s per step. The integrated intensity for each reflection was obtained with a moving window ' technique [8] and 4 reference reflections were measured after every 50 reflections in order to monitor any gradual variations in the experimental conditions. The sums of the intensities of the reference reflections were used to scale the observed intensities by interpolation between groups of reference reflections.

Intensity data were collected for the $\pm h$, $-k$, $\pm l$ reflections over the range $1° \le \theta \le 65°$ and for the $\pm h$, k, $\pm l$ reflections over the range $1° \le \theta \le 40°$. Merging of the two sets of data yielded 1 250 independent reflections of which 980 had $I \ge 3\sigma(I)$ and were thereby classified as significant; the overall residual for the 559 reflections measured more than once was 3.7%. Lorentz and polarisation corrections were applied to all reflections and empirical absorption corrections were obtained by the method of North *et al.* [9] using several $0k0$ reflections.

Structure Solution and Refinement.—The structure was solved using a weighted multi-solution tangent formula refinement (MULTAN) [10] and refined by the method of full-matrix least-squares. Initially all atoms were treated isotropically and refinement using only the significant reflections yielded an R value of 0.103. A difference Fourier synthesis revealed the hydrogen atoms as diffuse electron-density maxima and in subsequent cycles these atoms were placed in calculated positions assuming a C–H bond length of 1.0 Å. No attempts were made to refine the positional or thermal parameters of the hydrogen atoms. Further refinement proceeded with all non-hydrogen atoms treated anisotropically to yield final R values of 0.071 for the significant reflections and 0.088 for all reflections. Weights were assigned to the observed structure factors during the refinement using the scheme $w = a_0$ if $F_0 \le 20$ otherwise $w = [1 - \exp(-a_1\sin^2\theta/\lambda^2)]/(a_2 + |F_0| + a_3|F_0|^2)$. Values of $a_0 = 0.005$, $a_1 = 20$, $a_2 = 40$, and $a_3 = 0.2$ were used during the final cycle to give constancy in the values of $\Sigma w . \Delta^2$ when analysed in terms of batches of increasing $|F_0|$ and $\sin\theta/\lambda$. A final difference Fourier synthesis confirmed the correctness of the refinement.

Throughout the structure factor calculations the atomic scattering factors listed by Hanson *et al.*[11] were used and computations were performed on the IBM 360 computer at University College, London and the CDC 6600 computer at the University of London Computer Centre, using the Birkbeck College crystallographic program library. The least-squares refinement program is a modified version of that originally written by D. W. J. Cruickshank and J. G. F. Smith.

Observed and calculated structure factors, anisotropic thermal parameters, and calculated hydrogen atom co-ordinates are contained in a Supplementary Publication [SUP No. 23128 (10 pages)].*

* For details of the Supplementary Publications scheme, see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1,* 1980, Index Issue.

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