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18 January 1980

INTRODUCTION

The present volume continues the aim of Structure Reports to present critical accounts of all crystallographic structure determinations. Details of the arrangement in the volumes, symbols used etc. are given in previous volumes (e.g. 41B or 42A, pages vi-viii).

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18 January 1986

STRUCTURE REPORTS

SECTION III

ORGANIC COMPOUNDS

Edited by

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with the assistance of

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C. H. Morgan

T. J. R. Weakley

B. C. Williams

C. C. Wilson

D. W. Young

To find a particular organic or organometallic compound the subject index or formula index at the end of Part 2 of this volume should be used. The general arrangement is: aliphatic or open-chain compounds; open chains with N, S; benzene derivatives; cyclic hydrocarbons; condensed ring systems; heterocyclic compounds; carbohydrates; amino acids; natural products; molecular complexes; organometallic compounds - B, Si, P, As, Sb, groups IA, IIA, III, IV, VI; transition metal complexes - π -complexes, other ligands; inorganic anions which have organic counter ions. Only complete structure analyses are described, and those which have been reported in preliminary communications and for which details will appear at a later date, have not been described here.

ORGANIC COMPOUNDS

Edited by

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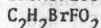
T. J. R. Weakley

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C. C. Wilson

D. W. Young

BROMOFLUOROACETIC ACID



R.D. ROGERS, B. KALYANARAMAN, M.S. DALTON, W. SMITH, L.D. KISPERS and J.L. ATWOOD, 1981. J. Cryst. Mol. Struct., 11, 105-111.

Monoclinic, $P2_1/c$, $a = 8.529$, $b = 5.632$, $c = 9.500$ Å, $\beta = 105.52^\circ$, $Z = 4$. Mo radiation, $R = 0.081$ for 654 reflexions.

The compound exists as centrosymmetric hydrogen-bonded dimers in the solid state (Fig. 1) with $\text{O}(1) \cdots \text{O}(2)$ 2.65(1) Å. Bond lengths in the molecule are $\text{Br}-\text{C}(1)$ 1.92(1), $\text{F}-\text{C}(1)$ 1.35(2), $\text{O}(1)-\text{C}(2)$ 1.21(1), $\text{O}(2)-\text{C}(2)$ 1.30(2) and $\text{C}(1)-\text{C}(2)$ 1.55(2) Å.

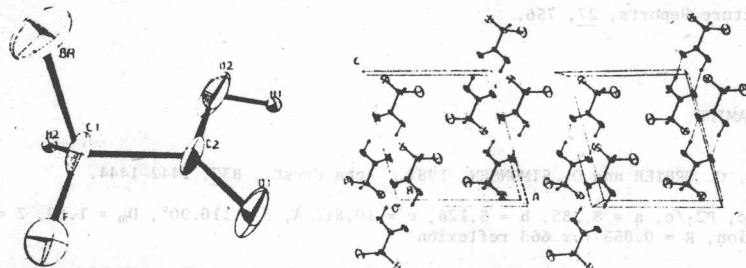


Fig. 1. $\text{C}_2\text{H}_2\text{BrFO}_2$: the molecular structure (left) and stereoscopic view of the unit cell contents (right).

MONOFLUOROACETAMIDE (at 20 K)



G.A. JEFFREY, J.R. RUBLE, R.K. McMULLAN, D.J. DeFREES and J.A. POPLE, 1981. Acta Cryst., B37, 1885-1890.

Triclinic, $P\bar{1}$, $a = 5.0974$, $b = 5.1531$, $c = 6.6501$ Å, $\alpha = 102.52^\circ$, $\beta = 101.33^\circ$, $\gamma = 99.54^\circ$, $Z = 2$. Neutrons, $\lambda = 1.0442$ Å, $R = 0.023$ for 1376 reflexions. [For previous study see 1.]

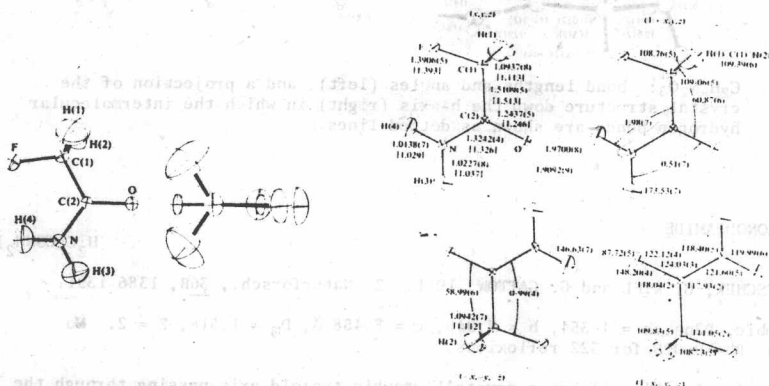


Fig. 1. $\text{C}_2\text{H}_4\text{FNO}$: a view normal to and in the plane of the molecule (left) and hydrogen bonding viewed normal to the molecular plane (right).

The crystal structure and the geometry of the non-hydrogen atoms confirms that reported in (1). The molecule (Fig. 1) has approximate m symmetry, with the C-F and C=O bonds trans, and the non-hydrogen atoms are coplanar within $\pm 0.0070(4)$ Å. Observed and thermally corrected bond lengths are: C-C 1.5109(5), 1.513; C-N 1.3242(2), 1.326; C=O 1.2437(5), 1.246; C-F 1.3906(5), 1.393; C-H 1.0937(8), 1.0942(7), 1.113, 1.112; and N-H 1.0227(8), 1.0138(7), 1.037, 1.029 Å. The crystal structure contains classic (H-N-C=O)₂ bonded dimers with almost linear N-H...O hydrogen bonds. These dimers are cross-linked into a network with longer N-H...O bonds which are not linear. Ab initio molecular-orbital calculations were carried out at the Hartree Fock 3-21G level and the theoretical results compared with those from the neutron experiment.

1. Structure Reports, 27, 756.

NITROACETAMIDE



N. THORUP, C. DREIER and O. SIMONSEN, 1981. Acta Cryst., B37, 1442-1444.

Monoclinic, $P2_1/c$, $a = 8.385$, $b = 5.126$, $c = 10.812$ Å, $\beta = 110.90^\circ$, $D_m = 1.59$, $Z = 4$. Mo radiation, $R = 0.053$ for 663 reflexions.

Bond lengths and angles in the molecule (Fig. 1) agree with generally expected values and indicate clearly that atom C(2) is sp^3 hybridized. The molecule fragments O(2), O(3), N(2), C(2) and O(1), N(1), C(1), C(2) are planar and have an interplane dihedral angle of 83.1° . Molecules are hydrogen-bonded to one another by N(1)-H...O(1) interactions of lengths 2.917 and 2.972 Å forming sheets of molecules nearly parallel to the planes (202).

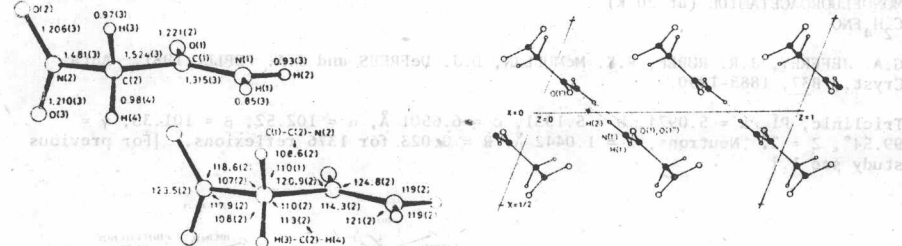
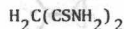


Fig. 1. C₂H₄N₂O₃: bond lengths and angles (left), and a projection of the crystal structure down the b-axis (right) in which the intermolecular hydrogen bonds are shown as dotted lines.

ETHYLMALONODIAMIDE



H. BLAWATSCHEK, G. KIEL and G. GATTOW, 1981. Z. Naturforsch., 36B, 1386-1391.

Rhombohedral, $P2nn$, $a = 4.354$, $b = 7.940$, $c = 8.458$ Å, $D_m = 1.518$, $Z = 2$. Mo radiation, $R = 0.028$ for 322 reflexions.

The molecule (Fig. 1) has a crystallographic twofold axis passing through the central carbon atom C(1) and the non-hydrogen atoms are approximately co-planar. The bond lengths C(2)-S(1), C(2)-C(1) and C(2)-N(1) are 1.674, 1.529 and 1.310 Å respectively and the angle C(2)-C(1)-C(2') is 109.2° . The molecules are connected by S...N bridges, of lengths in the range 3.491 to 3.553 Å, to form helices along the a-axis.

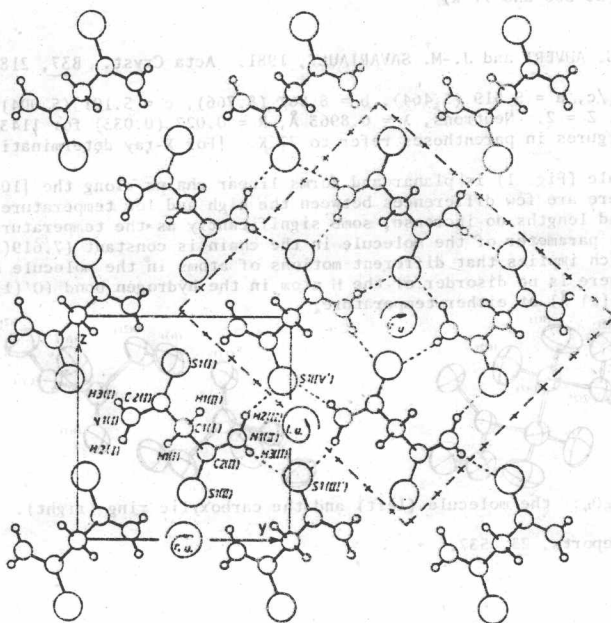


Fig. 1. $C_3H_6N_2S_2$: a projection of the crystal structure along the a -axis with the $S...H$ interactions shown as dashed lines and with the left-handed and right-handed helix axes marked l.u. and r.u. respectively.

POTASSIUM FLUORIDE DIDEUTEROSUCCINIC ACID

$C_4H_4D_2FKO_4$

$KF, [C_2H_4(COOD)_2]$

J. EMSLEY, D.J. JONES and R. KURODA, 1981. J. Chem. Soc. Dalton, 2141-2143.

Orthorhombic, $Pnam$, $a = 7.071$, $b = 5.575$, $c = 16.871$ Å, $Z = 4$. Mo radiation, $R = 0.029$ for 924 reflexions.

The crystal contains infinite chains of succinic acid molecules alternating with F^- ions (Fig. 1). Short asymmetric hydrogen bonds are present: $O...F$ 2.445, $O-D$ 0.885, $F...D$ 1.568 Å, $O-D...F$ 170.1, $D...F...D$ 128.5°. The K^+ ions are in irregular six-coordination, with bond lengths $K-F$ 2.664, 2.874, $K-O$ 2.818 ($\times 2$), 2.852 ($\times 2$) Å.

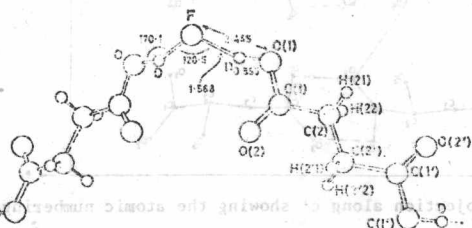


Fig. 1. $C_4H_4D_2FKO_4$: the short hydrogen bonds to the fluoride ion.

SUCCINIC ACID (at 300 and 77 K)

 $C_4H_4O_4$ $(CH_2COOH)_2$ J.-L. LEVIEL, G. AUVERT and J.-M. SAVARIAULT, 1981. *Acta Cryst.*, B37, 2185-2189.

Monoclinic, $P2_1/c$, $a = 5.519$ (5.464), $b = 8.862$ (8.766), $c = 5.101$ (5.004) Å, $\beta = 91.59$ (93.29)°, $Z = 2$. Neutrons, $\lambda = 0.8963$ Å, $R = 0.027$ (0.033) for 1143 (609) reflexions. Figures in parentheses refer to 77 K. [For X-ray determination see 1.]

The molecule (Fig. 1) is planar and forms linear chains along the [101] direction. There are few differences between the high and low temperature structures. However the bond lengths do increase, some significantly as the temperature increases. The translation parameter of the molecule in the chain is constant (7.619(2), 7.619(6) Å) which implies that different motions of atoms in the molecule are correlated. There is no disorder of the H atom in the hydrogen bond $O'(1)...O(2)$ 2.672(1), 2.678(2) Å at either temperature.



Fig. 1. $C_4H_4O_4$: the molecule (left) and the carboxylic ring (right).

1. *Structure Reports*, 23, 537.

DL-MALIC ACID

 $C_4H_6O_5$ J.F.J. VAN LOOCK, M. VAN HAVERE and A.T.H. LENSTRA, 1981. *Bull. Soc. Chim. Belg.*, 90, 161-166.

Monoclinic, Cc , $a = 13.053$, $b = 8.724$, $c = 4.878$ Å, $\beta = 103.31^\circ$, $Z = 4$. Mo radiation, $R = 0.055$ for 318 reflexions.

The malic acid molecule (Fig. 1) is in the trans conformation. Bond lengths and angles in the molecule agree with generally accepted values. The malic acid molecules form linear chains in which two short hydrogen bridges link the molecules in a head-to-tail fashion along the [101] direction. The cohesion between the chains is weak, based on van der Waals forces only. The two carboxyl functions show local disorder.

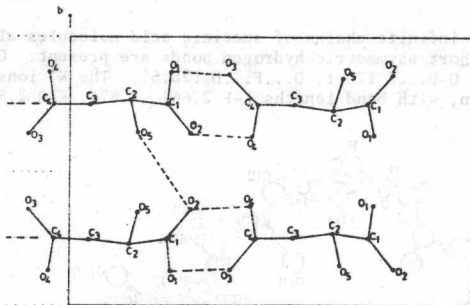
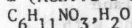


Fig. 1. $C_4H_6O_5$: projection along c^* showing the atomic numbering and crystal packing.

α -(ACETYL-D-AMINO)BUTYRIC ACID MONOHYDRATE

A. BAVOSO, E. BENEDETTI, B. DI BLASIO, G. MORELLI and C. PEDONE, 1981. *Acta Cryst.*, **B37**, 1132-1134.

Orthorhombic, $P2_12_12_1$, $a = 5.835$, $b = 7.756$, $c = 19.910$ Å, $Z = 4$. Cu radiation, $R = 0.045$ for 886 reflexions.

The bond lengths and valence angles in the molecule (Fig. 1) agree with generally accepted values. The six atoms of the amide group, including the hydrogen attached to the N atom, are coplanar and the amide bond is in the trans conformation. The dihedral angle between the N-acyl and carboxyl group is 97° . Packing is governed by hydrogen bonds involving the water molecule and all possible donor and acceptor sites of the peptide molecule.

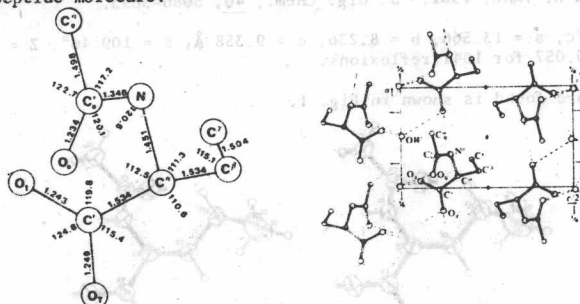
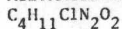


Fig. 1. $C_6H_{11}NO_3 \cdot H_2O$: the molecular geometry (left), and packing in the unit cell as viewed along the b-axis (right) with the hydrogen bonds represented by dashed lines.

ACETAMIDE HEMIHYDROCHLORIDE (neutron study, 120 K)



J.C. SPEAKMAN, M.S. LEHMANN, J.R. ALLIBON and D. SEMMINGSEN, 1981. *Acta Cryst.*, **B37**, 2098-2100.

Monoclinic, $P2_1/c$, $a = 6.291$, $b = 8.300$, $c = 7.931$ Å, $\beta = 113.43^\circ$, $Z = 2$. Neutrons, $\lambda = 0.8402$ Å, $R = 0.023$ for 882 reflexions (at 120 K).

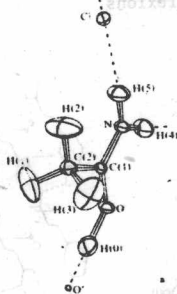


Fig. 1. $C_4H_{11}ClN_2O_2$: structure and atomic numbering, in which H(O) and Cl lie on crystallographic inversion centres.

The compound is properly represented by the formula $[C_2H_5NO \dots H \dots ONH_5C_2]^+ \cdot Cl^-$ with each ion centre on a point of inversion (Fig. 1). Bond lengths C(1)-O and C(1)-N are 1.263(2) and 1.308(1) Å respectively and differ from those in acetamide

(1). Except for H(1) and H(3) all the atoms lie within 0.09 Å from the plane C(1,2)N,O. The symmetric cation is held together by a strong hydrogen bond with O...O of length 2.426(3) Å. The Cl⁻ ion is involved in two pairs of N-H...Cl hydrogen bonds of lengths 3.2331(7) and 3.2800(7) Å.

1. Structure Reports, 46B, 5.

METHYL (Z)-2-ACETAMIDO-4-METHOXYBUT-2-ENOATE

C₈H₁₃NO₄

J.W. SCOTT, D.D. KEITH, G. NIX, D.R. PARRISH, S. REMINGTON, G.P. ROTH, J.M. TOWNSEND, D. VALENTINE and R. YANG, 1981. J. Org. Chem., 46, 5086-5093.

Monoclinic, P2₁/c, a = 13.566, b = 8.236, c = 9.358 Å, β = 109.46°, Z = 4. Cu radiation, R = 0.057 for 1641 reflexions.

The structure found is shown in Fig. 1.

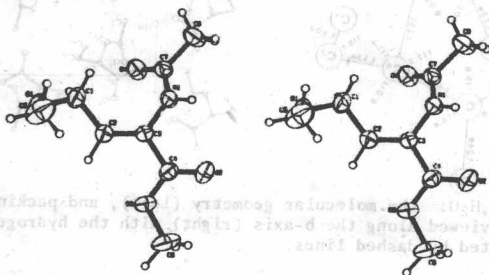


Fig. 1. Stereo-drawing of a C₈H₁₃NO₄ molecule.

3-COUMARIC ACID (3-HYDROXY-trans-CINNAMIC ACID)

C₉H₈O₃

S. RAGHUNATHAN and V. PATTABHI, 1981. Acta Cryst., B37, 1299-1301.

Monoclinic, P2₁/n, a = 5.402, b = 18.693, c = 7.973 Å, β = 98.28°, D_m = 1.395, Z = 4. Cu radiation, R = 0.072 for 1236 reflexions.

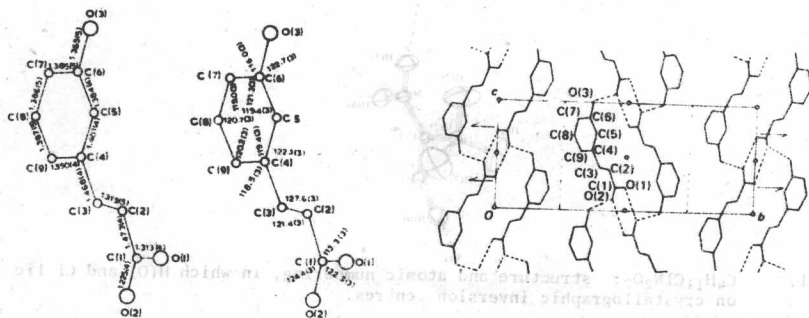


Fig. 1. C₉H₈O₃: bond lengths and angles (left) and the crystal structure viewed down [100] (right).

The phenyl ring of the molecule (Fig. 1) makes an angle of 6.8° with the plane of the carboxyl group. Bond distances C(1)-C(2) and C(3)-C(4) exhibit partial double bond character. C(4) is trans to C(1). In the crystal, molecules are cross-linked by O-H...O hydrogen bonds (2.80(1) Å) involving the terminal carboxyl O(2) and the central hydroxy O(3) to form infinite zig-zag chains which in turn are linked by O-H...O hydrogen bonds (2.65(1) Å) around the centre of symmetry forming dimers involving O(1) and O(2) of the carboxyl group. The sheets thus formed are held together by van der Waals forces.

METHYL m-CHLOROCINNAMATE
 $C_{10}H_9ClO_2$

R.G. BAUGHMAN and P.-J. YU, 1981. Cryst. Struct. Comm., **10**, 685-689.

Monoclinic, $P2_1/a$, $a = 7.728$, $b = 5.934$, $c = 21.022$ Å, $\beta = 99.85^\circ$, $Z = 4$. Cu radiation, $R = 0.050$ for 1058 reflexions.

The molecule (Fig. 1) is not quite planar because of slight rotations about the C(1)-C(7), C(8)-C(9), and C(9)-O(2) bonds. Dimensions are normal.

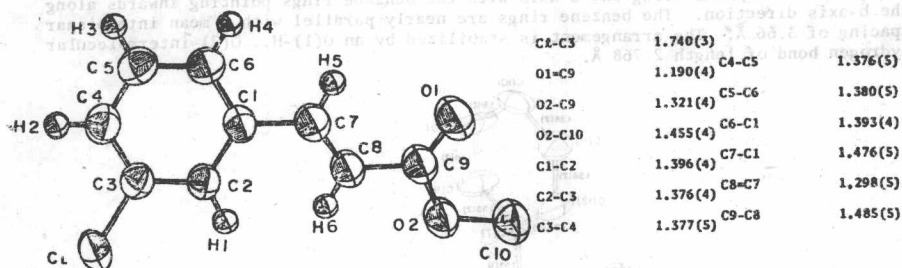


Fig. 1. Methyl m-chlorocinnamate.

(N-CYCLOHEXYL)-3,3-BIS(TRIFLUOROMETHYL)PYRUVAMIDE (at -120°C)
 $C_{11}H_{13}F_6NO_2$

A.I. JANOVSKIJ, A.E. KALININ, Ju.T. STRUCHKOV, É.G. BJKHOVSKAJA and I.L. KNUNJANC, 1981. Zh. Strukt. Khim., **22**(3), 125-130 [J. Struct. Chem., **22**, 410-413].

Orthorhombic, $Pna2_1$, $a = 23.661$, $b = 15.712$, $c = 10.424$ Å, $Z = 12$. Mo radiation, $R = 0.118$ for 1525 reflexions.

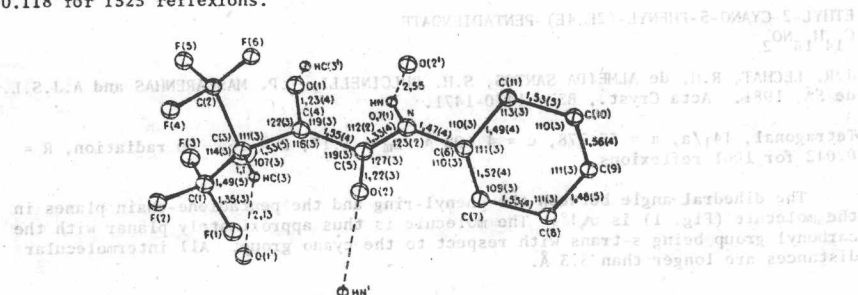


Fig. 1. $C_{11}H_{13}F_6NO_2$: a perspective view of one of the molecules showing averaged bond lengths and angles.

Within the limits of accuracy of the structure determination, all three crystallographically independent molecules have the same geometry (Fig. 1). The central fragment of the molecule, including the two carbonyl groups and the N atom, is nearly planar. The diketo group has the trans conformation and the cyclohexyl substituent the usual chair conformation. The three molecules are joined into chains along the b-axis by hydrogen bonds of the type C-H...O of lengths in the range 3.06 to 3.09 Å. There are also N-H...O contacts which constitute weak hydrogen bonds with H...O distances of 2.42, 2.51 and 2.72 Å. The interactions between these chains are van der Waals in nature.

4-HYDROXY-4-PHENYLHEXANAMIDE



E.E. CASTELLANO, J.Z. SCHPECTOR and G. CARVAJAL, 1981. *Acta Cryst.*, B37, 284-286.

Orthorhombic, Pcca, $a = 23.025$, $b = 10.366$, $c = 10.069$ Å, $D_m = 1.14$, $Z = 8$. Mo radiation, $R = 0.082$ for 707 reflexions.

All distances in the molecule (Fig. 1) are within the expected range except those of the planar benzene ring which are rather short probably due to libration. The molecules form chains along the a-axis with the benzene rings pointing inwards along the b-axis direction. The benzene rings are nearly parallel with a mean interplanar spacing of 3.66 Å. The arrangement is stabilized by an O(1)-H...O(2) intermolecular hydrogen bond of length 2.768 Å.

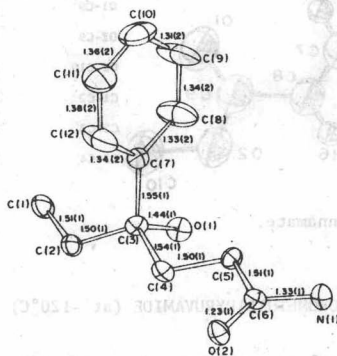
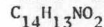


Fig. 1. $\text{C}_{12}\text{H}_{17}\text{NO}_2$: perspective view of and bond distances in the molecule.

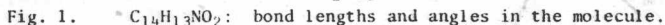
ETHYL-2-CYANO-5-PHENYL-(2E,4E)-PENTADIENOATE



J.R. LECHAT, R.H. de ALMEIDA SANTOS, S.H. PULCINELLI, Y.P. MASCARENHAS and A.J.S.L. de SÁ, 1981. *Acta Cryst.*, B37, 1470-1471.

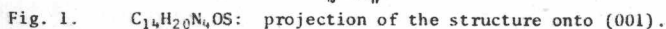
Tetragonal, $I4_1/a$, $a = 33.278$, $c = 4.608$ Å, $D_m = 1.17$, $Z = 16$. Cu radiation, $R = 0.042$ for 1061 reflexions.

The dihedral angle between the phenyl-ring and the pentadiene-chain planes in the molecule (Fig. 1) is 6.4°. The molecule is thus approximately planar with the carbonyl group being s-trans with respect to the cyano group. All intermolecular distances are longer than 3.3 Å.

 $C_{14}H_{20}N_4OS$

Monoclinic, $P2_1/n$, $a = 15.338$, $b = 11.469$, $c = 8.795$ Å, $\gamma = 95.87^\circ$, $Z = 4$. Mo radiation. $R = 0.071$ for 1540 reflexions.

In the molecule (Fig. 1) the central four-atom fragments S,N(4),C(1),N(1) and N(2),C(2,3,4) are each practically planar and the dihedral angle between these planes is 13.3°. The benzene ring is slightly deformed from planarity and the angle between its mean plane and that of the thiocarbamide fragment is 54.8°. The amide group is planar and is rotated through an angle of 43.3° about the C(2)-C(4) bond with respect to the N(2),C(2,3,4) plane. Interatomic distances agree well with accepted values. There is one possible intermolecular hydrogen bond (2.99 Å) between the hydrazine NH group and the O atom of a neighbouring molecule.



α -HYDROXY- β -[(2-METHYL-1-OXO-2-BUTENYL)AMINO]BENZENEPROPANOIC ACID METHYL ESTER
 $C_{15}H_{19}NO_4$

R.W. MILLER, R.G. POWELL, C.R. SMITH, E. ARNOLD and J. CLARDY, 1981. J. Org. Chem., 46, 1469-1474.

Monoclinic, $P2_1$, $a = 7.403$, $b = 9.633$, $c = 11.675$ Å, $\beta = 63.59^\circ$, $Z = 2$. Cu radiation, $R = 0.070$ for 1050 reflexions.

The X-ray structure analysis established the identity of the molecule to be that shown in Fig. 1. There is an intermolecular hydrogen bond from O(13)H to O(6') of 2.73 Å. Bond lengths and angles have the expected values.

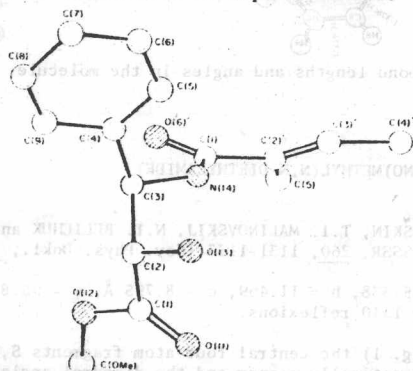


Fig. 1. Perspective drawing of the $C_{15}H_{19}NO_4$ molecule.

BIS(S-METHYL) (22,4E,6Z)-2,3,6,7-TETRAMETHOXY-4,5-BIS(METHYLTHIO)OCTA-2,4,6-TRIENETHIOATE
 $C_{16}H_{24}O_6S_4$ (I)

S-METHYL (3Z)-3-METHOXY-4-(METHYLTHIO)-2-OXOBUT-3-ENETHIOATE
 $C_7H_{10}O_3S_2$ (II)

C.H. EUGSTER, M. BALMER, R. PREWO and J.H. BIERT, 1981. Helv. Chim. Acta, 64, 2636-2644.

I. Triclinic, $P\bar{1}$, $a = 7.594$, $b = 7.803$, $c = 10.328$ Å, $\alpha = 80.59^\circ$, $\beta = 82.07^\circ$, $\gamma = 61.03^\circ$, $Z = 1$. Mo radiation, $R = 0.048$ for 1638 reflexions.

II. Monoclinic, $P2_1/c$, $a = 4.080$, $b = 12.839$, $c = 19.425$ Å, $\beta = 106.85^\circ$, $Z = 4$. Mo radiation, $R = 0.059$ for 2844 reflexions.

The X-ray structure determinations established the structures of I and II which are shown in Fig. 1. Molecule I lies on an inversion centre. Neither the conjugated double bond system nor the endiolether group are planar. The C(1)-C(2) bond is twisted 18° from planarity and the torsion angle C(2)-C(3)-C(4)-C(4') is 78.4° . The twisting about C(1)-C(2) and C(3)-C(4) reduces contact between S(4) and O(3'). Both enone groups lie in parallel planes. Apart from the methyl group on O(3), molecule II is essentially planar. The C(1)-C(2)-C(3)-C(4) torsion angle is -11.6° and the O(1)...H(4) distance is 2.22 Å.