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Structures of Ethyl 3-Amino-2-cyanocrotonate, $C_7H_{10}N_2O_2$, and Ethyl 3-Amino-2-cyanodithiocrotonate, $C_7H_{10}N_2S_2$

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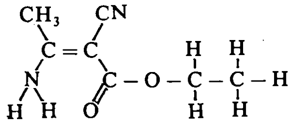
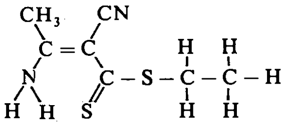
Abstract. $C_7H_{10}N_2O_2$: $M_r = 154{\cdot}2$, monoclinic, $C2/c$, $a = 9{\cdot}437\,(2)$, $b = 16{\cdot}408\,(3)$, $c = 10{\cdot}453\,(5)$ Å, $\beta = 90{\cdot}68\,(2)°$, $V = 1618{\cdot}4\,(14)$ Å^3, $Z = 8$, $D_x = 1{\cdot}265\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}1017$ mm^{-1}, $F(000) = 656$, $T = 296$ K, final $R = 0{\cdot}085$ for 1442 reflections. $C_7H_{10}N_2S_2$: $M_r = 186{\cdot}3$, monoclinic, $C2/c$, $a = 26{\cdot}192\,(3)$, $b = 5{\cdot}038\,(2)$, $c = 14{\cdot}077\,(2)$ Å, $\beta = 89{\cdot}467\,(10)°$, $V = 1857{\cdot}5\,(12)$ Å^3, $Z = 8$, $D_x = 1{\cdot}332\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}496$ mm^{-1}, $F(000) = 784$, $T = 296$ K, final $R = 0{\cdot}063$ for 2105 reflections. The molecular structures of the isomorphous compounds are compared. The molecules of $C_7H_{10}N_2O_2$ and $C_7H_{10}N_2S_2$ are chelated to form a six-membered ring *via* intramolecular N—H···O and N—H···S hydrogen bonds respectively. A comparison of the bond distances suggests that the N—H···S hydrogen bond is stronger than the N—H···O. Both molecules with their three-membered chains and the electronegative substituents at the chain ends tend to a polymethinic state. One-dimensionally extended chains of the molecules and two-dimensionally extended nets of the molecules in the crystal structures of $C_7H_{10}N_2S_2$ and $C_7H_{10}N_2O_2$, respectively, are produced by intermolecular hydrogen bonds.

Introduction. Spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, dipole measurement) and the reaction behaviour of the two activated ethenes ethyl 3-amino-2-cyanocrotonate (ACC) and ethyl 3-amino-2-cyanodithiocrotonate (ACD) have been studied (Kreutzmann, 1980; Michalik & Kreutzmann, 1983).

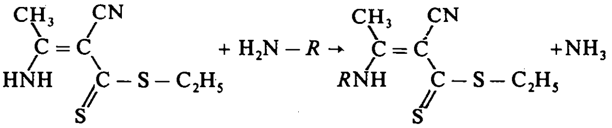


ACC



ACD

Noteworthy differences of reactivity exist between the two compounds. ACD reacts with primary aliphatic amines with replacement of the amino group in position C(5) (for atom numbering see Figs. 1 and 2), whereas ACC under the same conditions does not react (R is an aliphatic group):



Spectroscopic data do not explain completely the different reaction behaviours. X-ray crystal structure analyses of ACD and ACC should elucidate any peculiarities of these compounds and contribute to the explanation of unanswered questions.

Experimental. Specimens as reported earlier (Kreutzmann, 1979, 1980). Colourless prisms of ACC and yellow prisms of ACD (0·31 × 0·4 × 0·6 mm and 0·13 × 0·24 × 0·60 mm, respectively) obtained by slow evaporation of a dimethyl sulphoxide solution, $T = 293$ K. Hilger & Watts diffractometer. Unit cell: 12 (ACC) and 12 (ACD) reflections, least-squares refinement. ω–2θ step scan, 40 steps of 1 s, $\Delta\omega = 0{\cdot}02°$ up to $\theta_{\max} = 25°$ (ACC) and 27·5° (ACD), graphite-monochromatized Mo $K\alpha$ radiation, $T = 296$ K. Lp correction, no absorption correction. Unique measured reflections (hkl and $\bar{h}kl$): 1484 (ACC), 2148 (ACD). In each case two standard reflections measured every 50 reflections: no significant variations. Systematic extinctions of ACC and ACD: for all reflections with $h + k$ odd and for $h0l$ with l odd. Structure determined by direct methods (*MULTAN*76; Main, Lessinger, Woolfson, Germain & Declercq, 1976). Full-matrix least-squares refinement of positional and anisotropic thermal parameters minimizing $\sum w(\Delta F)^2$;

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unit weights. H atoms of CH_2 and CH_3 groups placed in calculated positions, staggered geometry assumed; H atoms of NH_2 from $\Delta\rho$ map (*SHELX*; Sheldrick, 1976); all H atoms isotropic. 42 (ACC) and 43 (ACD) reflections with $F_o \leq 3\sigma(F_o)$ (σ from counting statistics) omitted in the final stages of refinement. Final $R = 0{\cdot}085$ (ACC) and $0{\cdot}063$ (ACD); $(\Delta/\sigma)_{\max} = 0{\cdot}44$ (ACC), 0·48 (ACD); difference syntheses showed no significant features. BESM 6 computer. Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

Discussion. Atomic parameters are given in Tables 1 and 2.* Bond distances and angles of ACC and ACD are given in Figs. 1 and 2 respectively. The molecules are nearly planar with maximum deviations of 0·037 (4) (ACC) and 0·075 (3) Å (ACD) of nonhydrogen atoms from the mean plane determined by all nonhydrogen atoms. The intramolecular N—H···*X* (*X*=O,S) hydrogen bond causes the sterically favoured six-membered ring formation. Most bond distances and angles of ACC and ACD are quite similar and agree within the limits of the standard deviations. Deviations exist obviously between the distances involving O and S, and between the angles C(3)—C(4)—C(5) and *X*(2)—C(3)—C(4) (*X*=O,S). The differences in the angles mentioned may be caused by steric hindrance in connection with the different space requirements of O and S, influencing primarily the hydrogen-bond distances of the six-membered chelate ring. In ACC and ACD the two canonical structures (1) and (2) should contribute to the electronic state of both molecules.

Table 1. *ACC: fractional coordinates* ($\times 10^4$), U_{eq} *values for nonhydrogen atoms and* U_{iso} *values for hydrogen atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso} ($Å^2 \times 10^3$)
O(1)	2305 (2)	901 (1)	2430 (2)	59
O(2)	829 (3)	379 (1)	952 (3)	72
N(1)	−538 (3)	1444 (2)	−578 (3)	60
N(2)	2284 (3)	2936 (2)	2393 (3)	71
C(1)	3604 (4)	107 (2)	3934 (4)	83
C(2)	2576 (4)	68 (2)	2844 (4)	66
C(3)	1369 (3)	974 (2)	1457 (3)	54
C(4)	1082 (3)	1799 (2)	1094 (3)	49
C(5)	125 (4)	1997 (2)	104 (3)	50
C(6)	−168 (4)	2871 (2)	−229 (4)	63
C(7)	1749 (3)	2433 (2)	1802 (3)	54
H(1)	3836 (4)	−502 (2)	4265 (4)	60†
H(10)	3146 (4)	456 (2)	4701 (4)	60†
H(100)	4570 (4)	396 (2)	3628 (4)	60†
H(2)	1603 (4)	−217 (2)	3142 (4)	60†
H(20)	3027 (4)	−276 (2)	2068 (4)	60†
H(6)	−587 (48)	2954 (30)	−1162 (25)	127 (18)
H(60)	−223 (52)	3206 (23)	623 (27)	107 (15)
H(600)	847 (32)	3093 (31)	−532 (51)	136 (19)
H(N1)	−480 (43)	834 (12)	−403 (42)	103 (15)
H(N10)	−984 (37)	1607 (23)	−1421 (24)	84 (13)

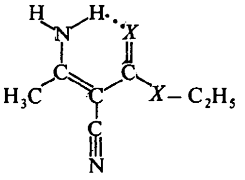
† Atom not refined.

Table 2. *ACD: fractional coordinates* ($\times 10^4$), U_{eq} *values for nonhydrogen atoms and* U_{iso} *values for hydrogen atoms*

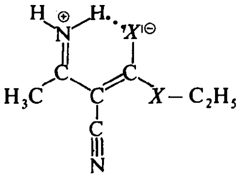
$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso} ($Å^2 \times 10^3$)
S(1)	4015 (1)	−283 (2)	5552 (1)	56
S(2)	4112 (1)	−1101 (2)	3467 (1)	61
N(1)	3361 (1)	2737 (6)	2644 (2)	57
N(2)	3068 (1)	4176 (6)	5904 (2)	66
C(1)	4647 (2)	−3717 (9)	6415 (3)	81
C(2)	4495 (1)	−2849 (6)	5437 (2)	57
C(3)	3831 (1)	427 (5)	4385 (2)	44
C(4)	3433 (1)	2370 (5)	4330 (2)	44
C(5)	3229 (1)	3496 (6)	3504 (2)	48
C(6)	2837 (1)	5659 (7)	3563 (3)	60
C(7)	3229 (1)	3392 (6)	5203 (2)	48
H(1)	4934 (2)	−5251 (9)	6359 (3)	70†
H(10)	4317 (2)	−4483 (9)	6789 (3)	70†
H(100)	4800 (2)	−2044 (9)	6798 (5)	70†
H(2)	4824 (1)	−2076 (9)	5061 (2)	55†
H(20)	4341 (1)	−4515 (6)	5051 (2)	55†
H(6)	2531 (12)	5145 (94)	3995 (26)	125 (15)
H(60)	2734 (16)	6717 (88)	2932 (22)	147 (17)
H(600)	2899 (19)	6839 (98)	4188 (20)	140 (17)
H(N1)	3623 (12)	1354 (61)	2545 (26)	90 (12)
H(N10)	3223 (11)	3721 (60)	2104 (16)	66 (9)

† Atom not refined.

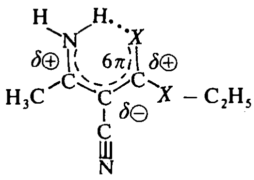


(1)



(2)

The C atoms C(3), C(4) and C(5) together with the more electronegative N(1) and *X*(2) (*X*=O,S) at the ends of the chains represent a polymethine-like state which is characterized by alternating π-electron densities (Dähne & Kulpe, 1977).



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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38885 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

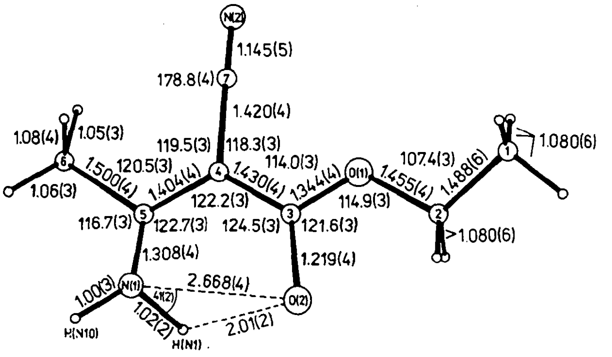

Fig. 1. Bond lengths (Å) and angles (°) for ACC, with standard deviations in parentheses.

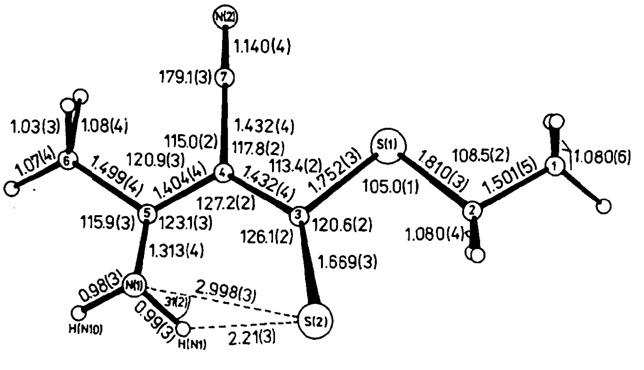

Fig. 2. Bond lengths (Å) and angles (°) for ACD, with standard deviations in parentheses.

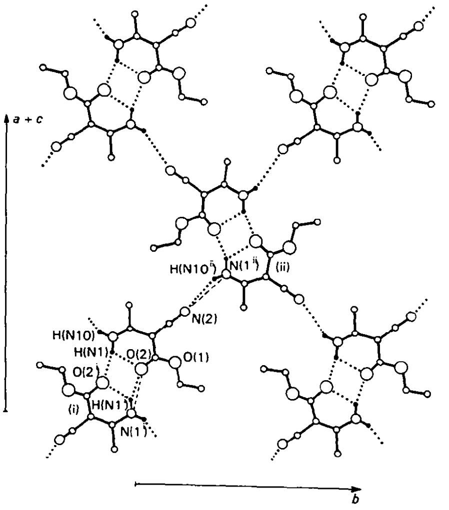

Fig. 3. ACC: schematic representation of molecular network formed by the intermolecular hydrogen bonds. Symmetry-equivalent positions are denoted by (i) $\bar{x},\bar{y},\bar{z}$ and (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$. [N(1^i)···O(2) 3·030 (4), H(N1^i)···O(2) 2·10 (2) Å; N(1^{ii})···N(2) 3·106 (4), H(N10^{ii})···N(2) 2·17 (3) Å.]

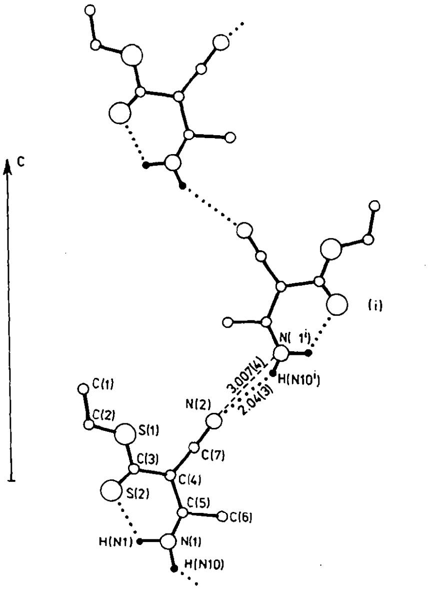

Fig. 4. ACD: schematic representation of the molecular chain formed by the intermolecular hydrogen bonds (distances in Å). Symmetry-equivalent positions are denoted by (i) x, $1-y$, $\frac{1}{2}+z$.

The packing of the molecules is essentially determined by the intermolecular hydrogen bonds. In ACC two kinds of intermolecular hydrogen bonds [N(1^i)–H(N1^i)···O(2) and N(1^{ii})–H(N10^{ii})···N(2)] produce two-dimensional nets, see Fig. 3. The intermolecular hydrogen bond N(1)–H(N1)···O(2^i) together with the intramolecular hydrogen bond N(1)–H(N1)···O(2) represent a bifurcated hydrogen bond and cause dimerization. In ACD dimers do not exist. This may be caused by difficulties in the formation of bifurcated hydrogen bonds with S participation. The second type of intermolecular hydrogen bond observed in ACC between the amino group and N of the cyano group exists also in ACD and causes a one-dimensional connection of the molecules, Fig. 4.

The intramolecular N–H···S hydrogen bond with N···S = 2·998 (3), H···S = 2·21 (3) Å and angle H–N–S = 31 (2)° is very short and strong. The mean N···S hydrogen-bond length determined from 53 organic crystal structures [3·42 (11) Å; Kuleshova & Zorkii, 1981] markedly exceeds the bond length in ACD. Donohue (1969) surveyed N–H···S hydrogen bonds and found a distribution range for N···S distances of from 3·25 to 3·55 Å combined with a nearly collinear arrangement of the three atoms involved. Therefore, the N–H···S hydrogen bond found in ACD is one of the shortest known. This N–H···S hydrogen bond may be induced by steric constraints favouring the polar limit structure (2) and thereby making possible the formation of the strong N–H···S hydrogen bond. Of special interest, in connection with the reaction behaviour, is a comparison of the hydrogen bonds in ACC and ACD. A measure of the strength of the N—H···*X* hydrogen bonds (*X*=S,O) discussed here is the shortening of the N···*X* distance below the sum of the van der Waals radii involved (Schuster, Zundel & Sandorfy, 1976). The N—H···O hydrogen bond in the crystal structure of ACC has an N···O distance of 2·668 (4) Å which is 0·26 Å shorter than the sum of the van der Waals radii [2·93 Å; van der Waals radii given by Kitaigorodskii (1971) were used]. The N—H···S hydrogen bond in the crystal structure of ACD with an N···S distance of 2·998 (3) Å is 0·6 Å shorter than the sum of the van der Waals radii (3·59 Å). Furthermore, in N—H···S the H atom is closer to the N···*X* connection line than in the case of N—H···O. Both suggest the surprising feature that a hydrogen bond of type N—H···S is stronger than that of type N—H···O. The ability of thiocarboxy S to form such an unusually strong hydrogen bond is in agreement with IR and NMR measurements. Correlation between the different hydrogen bonds and the reaction behaviour of ACC and ACD is possible.

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The Structure of 1-(Tetracyclo[5.4.0.0^{3,8}.0^{4,8}]undec-5-en-9-yl)ethanol, $C_{13}H_{18}O$

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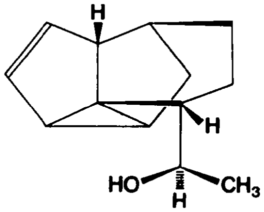
Abstract. $M_r = 190{\cdot}3$, rhombohedral, $R\bar{3}$, $a = 26{\cdot}371$ (3), $c = 8{\cdot}374$ (2) Å (hexagonal axes, obverse setting), $U = 5043$ (2) Å^3, $Z = 18$, $D_m = 1{\cdot}13$ (flotation), $D_x = 1{\cdot}128$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}75$ cm^{-1}, $F(000) = 1872$, $T = 295$ K, $R = 0{\cdot}038$, $R_w = 0{\cdot}033$ for 1160 counter reflections. The outstanding feature in this highly strained molecule is a C—C—C bond angle of 140·2 (2)°.



(I)

Introduction. The *meta*-photocycloaddition of olefins to arenes first reported by Wilzbach & Kaplan (1966) and by Bryce-Smith, Gilbert & Orger (1966) finds extensive application in five-membered ring synthesis. The intramolecular version of this reaction in bichromophoric molecules discovered by Morrison & Ferree (1969) serves to provide cycloadducts that could be used to synthesize a variety of natural products. The title compound (I) appeared as one of several photoproducts from photolysis of *threo*-3-phenyl-6-hepten-2-ol in spectroscopic-grade *n*-hexane with a high-pressure Hg lamp.

Experimental. Single crystals grown by slow evaporation of a solution in hexane/dichloromethane/*tert*-butyl methyl ether mixture were provided by Dr R. Astik. Cell parameters obtained from diffractometer settings. Crystals showed a tendency to decay rapidly and four had to be used to collect the full data set; $2\theta_{\max} = 50°$, ω scans of variable scan rate, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections monitored every hour and measurements with a crystal stopped when the intensity of any of them dropped to below 85% of the starting value; decay of the intensity check

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