

The carboxylic ester group has the usual conformation with C(3), O(10), C(11), O(12) and C(13) approximately in one plane (largest deviation 0.03 Å) and O(10)—C(3) *syn* with respect to C(11)—O(12) about the bond O(10)—C(11). The benzene ring is planar within the limits of accuracy with an average C—C distance of 1.386 Å. The terminal bond of the *n*-butyl group is rather short (1.48 Å) probably due to the extra large thermal motion of the terminal methyl group.

The packing is effected by normal van der Waals interactions.

Our thanks are due to Dr C. F. Moorhoff for suggesting the investigation and providing the crystals.

References

CAHN, R. S., INGOLD, C. K. & PRELOG, V. (1956). *Experientia*, **12**, 81–94.

FODOR, G. (1955). *Experientia*, **11**, 129–140.

GABE, E. J. & BARNES, W. H. (1963). *Acta Cryst.* **16**, 796–801.

HUBER, C. S., FODOR, G. & MANDAVA, N. (1971). *Can. J. Chem.* **49**, 3258–3271.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LEGER, J. M., GADRET, M. & CARPY, A. (1978). *Acta Cryst.* **B34**, 3705–3709.

MOORHOFF, C. F. (1975). *Planta Med.* **28**, 106–108.

PAULING, P. & PETCHER, T. J. (1969). *Chem. Commun.* pp. 1001–1002.

SCHENK, H., MACGILLAVRY, C. H., SKOLNIK, S. & LAAN, J. (1967). *Acta Cryst.* **23**, 423–426.

STEWART, J. M. (1976). Editor, the XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

VISSER, J. W., MANASSEN, J. & DE VRIES, J. C. (1954). *Acta Cryst.* **7**, 288–291.

Acta Cryst. (1982). **B38**, 335–337

(2*E*,4*E*)-2-Cyano-4-methyl-5-thiocyanato-2,4-hexadienoic Acid Ethyl Ester

BY P. KNUUTILA AND H. KNUUTILA

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, 40100 Jyväskylä, Finland

AND B. SCHULZE, M. MÜHLSTÄDT AND J. KAISER*

Department of Chemistry, Karl-Marx-University of Leipzig, Liebigstrasse 18, 7010 Leipzig, German Democratic Republic

(Received 11 February 1981; accepted 1 July 1981)

Abstract. C₁₁H₁₂N₂O₂S, monoclinic, *P*2₁/*c*, *a* = 4.551 (3), *b* = 19.846 (13), *c* = 13.358 (8) Å, β = 90.49 (5)°, *D*_o = 1.32, *D*_c = 1.300 Mg m⁻³, *Z* = 4; *R* = 0.046 for 1178 reflections with *I* > 2σ(*I*). The most important feature of the structure is the presence of a substituted (*E*)-*s-trans*-(*E*)-1,3-butadiene.

Introduction. In continuation of our research on β-thiocyanatovinylcarbonyl compounds (Mühlstädt, Brämer & Schulze, 1976; Schulze, Brämer, Kleinpeter & Mühlstädt, 1976), we prepared 2-cyano-4-methyl-5-thiocyanato-2,4-hexadienoic acid ethyl ester (CMTHCE) by reaction of (*E*)-α-methyl-β-thiocy-

anacrotonaldehyde with ethyl cyanoacetate in the presence of piperidine acetate (Schulze, Mühlstädt, Baldauf & Brämer, 1977). We previously suggested the existence of an (*E*)-*s-trans*-(*E*) conformation for the possible stereoisomeric forms of CMTHCE on the basis of ¹H NMR spectroscopy from the H(3) proton chemical shift, the Eu(fod)₃[†]-produced paramagnetic signal shifts of the ¹H resonances and UV spectroscopy. However, according to the fragment behaviour in the mass spectrum (Herzschuh, Schulze & Mühlstädt, 1981) other isomers are possible. Therefore, an X-ray structure analysis was undertaken to confirm the spectroscopic assignment of the stereochemistry.

[†] Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)-europium(III).

* To whom correspondence should be addressed.

The unit-cell parameters were obtained from the 2θ values of 15 high-order reflections, measured on a Syntex $P2_1$ diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). 2762 independent reflections ($5 \leq 2\theta \leq 55^\circ$) were collected at room temperature with the $\theta/2\theta$ scan technique and scan rate ranging from 1.00 to $15.0^\circ \text{ min}^{-1}$ depending upon the peak intensity; 1178 of these with $I > 2.0\sigma(I)$ were used in the analysis. Corrections were applied for Lorentz and polarization effects but not for absorption and anomalous dispersion.

The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). An E map based on 159 E values ($E > 1.0$) gave all heavy-atom positions. All calculations were performed on a UNIVAC 1100 computer at the University of Jyväskylä with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1976).

Scattering factors for the non-hydrogen atoms were from Cromer & Mann (1968) and those for H atoms from Stewart, Davidson & Simpson (1965). Full-matrix least-squares refinement of all non-hydrogen atoms with isotropic thermal parameters led to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.15$ and subsequent block-diagonal refinement with anisotropic temperature factors reduced R to 0.076. At this point all hydrogen atoms were located from a difference map. Three least-squares cycles, in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters, then reduced R to 0.0458 for 1178 reflections and 194 parameters. Unit weights were used. The final difference map was featureless.

Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1;* distances and angles are in Table 2. The numbering of the atoms is shown in Fig. 1 and a stereoscopic drawing of the unit cell in Fig. 2 (Johnson, 1965).

Table 1. Final positional parameters for non-hydrogen atoms with *e.s.d.*'s in parentheses and U_{eq} ($\text{\AA}^2 \times 10^3$)

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^* |
|-------|-------------|-------------|-------------|------------|
| S(1) | 0.6544 (1) | 0.09806 (3) | 0.99700 (3) | 55.5 (3) |
| O(1) | -0.2114 (3) | 0.31792 (7) | 0.76662 (7) | 88 (1) |
| O(2) | -0.3275 (3) | 0.39270 (6) | 0.88522 (7) | 65 (1) |
| N(1) | -0.0344 (5) | 0.3569 (1) | 1.052 (1) | 113 (2) |
| N(2) | 0.9607 (4) | 0.0114 (1) | 0.8687 (1) | 94 (1) |
| C(1) | -0.1955 (4) | 0.3385 (1) | 0.8514 (1) | 59 (1) |
| C(2) | -0.0188 (3) | 0.3027 (1) | 0.9296 (1) | 52 (1) |
| C(3) | 0.1331 (4) | 0.2488 (1) | 0.9052 (1) | 52 (1) |
| C(4) | 0.3102 (4) | 0.2027 (1) | 0.9634 (1) | 56 (1) |
| C(5) | 0.4608 (4) | 0.1543 (1) | 0.9176 (1) | 51 (1) |
| C(6) | 0.4843 (5) | 0.1432 (1) | 0.8059 (1) | 72 (1) |
| C(7) | -0.5039 (5) | 0.4315 (1) | 0.8134 (1) | 72 (1) |
| C(8) | -0.6362 (5) | 0.4872 (1) | 0.8687 (1) | 88 (2) |
| C(9) | -0.0296 (5) | 0.3326 (1) | 1.0293 (1) | 73 (1) |
| C(10) | 0.3206 (5) | 0.2089 (1) | 1.0777 (1) | 78 (1) |
| C(11) | 0.8313 (4) | 0.0480 (1) | 0.9153 (1) | 68 (1) |

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 2. Bond distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

| | | | |
|------------|-----------|-----------------|-----------|
| S(1)—C(5) | 1.770 (2) | C(5)—S(1)—C(11) | 102.8 (1) |
| S(1)—C(11) | 1.686 (2) | C(1)—O(2)—C(7) | 117.1 (1) |
| O(1)—C(1) | 1.206 (2) | O(1)—C(1)—O(2) | 125.2 (2) |
| O(2)—C(1) | 1.314 (2) | O(1)—C(1)—C(2) | 121.6 (2) |
| O(2)—C(7) | 1.465 (2) | O(2)—C(1)—C(2) | 113.3 (1) |
| N(1)—C(9) | 1.122 (2) | C(1)—C(2)—C(3) | 119.7 (1) |
| N(2)—C(11) | 1.127 (3) | C(1)—C(2)—C(9) | 115.0 (1) |
| C(1)—C(2) | 1.492 (2) | C(3)—C(2)—C(9) | 125.3 (1) |
| C(2)—C(3) | 1.316 (2) | C(2)—C(3)—C(4) | 132.4 (1) |
| C(2)—C(9) | 1.460 (2) | C(3)—C(4)—C(5) | 119.8 (1) |
| C(3)—C(4) | 1.443 (2) | C(3)—C(4)—C(10) | 119.9 (1) |
| C(4)—C(5) | 1.332 (2) | C(5)—C(4)—C(10) | 120.3 (2) |
| C(4)—C(10) | 1.532 (2) | S(1)—C(5)—C(4) | 115.8 (1) |
| C(5)—C(6) | 1.512 (2) | S(1)—C(5)—C(6) | 117.4 (1) |
| C(7)—C(8) | 1.463 (3) | C(4)—C(5)—C(6) | 126.8 (1) |
| | | O(2)—C(7)—C(8) | 107.0 (1) |
| | | N(1)—C(9)—C(2) | 178.4 (2) |
| | | S(1)—C(11)—N(2) | 173.3 (2) |

* Lists of structure factors, anisotropic thermal parameters of non-hydrogen atoms, hydrogen-atom parameters, and bond distances and angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36184 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

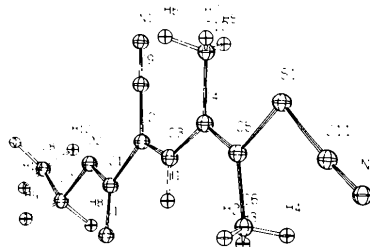


Fig. 1. Numbering of the atoms.

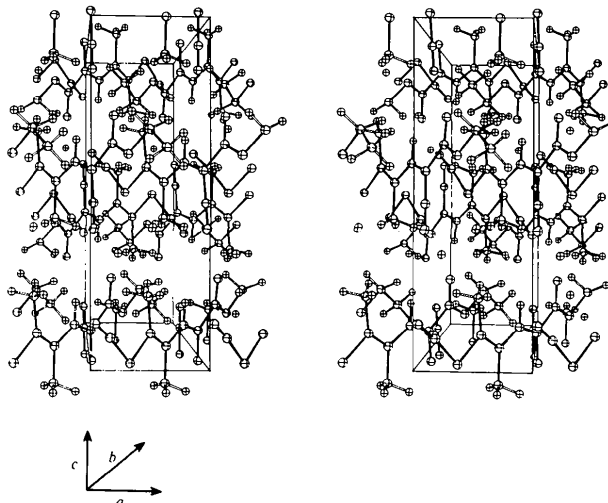


Fig. 2. Stereoscopic drawing of the unit cell.

Discussion. The condensation of aromatic aldehydes with a cyanoacetic acid ester gives stereospecific *E* isomers (Baker & Howes, 1953). However, when unsymmetrical ketones are condensed with a cyanoacetic acid ester, a mixture of *E* and *Z* isomers is obtained (Hayashi, 1966; Hayashi, Igarashi, Hayashi & Midorikava, 1965; Cernayova, Kovac, Dandarova & Rajniakova, 1977) in which the isomer with a *trans* relation between the more bulky substituent and the alkoxy carbonyl group predominates. The stereochemistry of the condensation products of aliphatic aldehydes with a cyanoacetic acid ester under Knoevenagel conditions has not yet been thoroughly investigated (Popp & Catala, 1961; Alexander & Cope, 1944; Astle & Zaslowsky, 1952; Mastagli, Lambert & Andric, 1956). Crotonaldehyde gives two isomers (Cawley, Evans & Farmer, 1930). The configurations of these products have not been established. Our present results for CMTHCE show unambiguously a substituted (*E*)-*s-trans*-(*E*) butadiene. All bond lengths lie within expected ranges, except for a significant shortening of C(3)–C(4) to 1.443(2) Å and are not discussed further. Bond angles are characteristic of tetrahedral and trigonal bonding. However, angle C(2)–C(3)–C(4) is widened to 132.4(1)° by steric interaction of the cyanide and methyl groups. The double bonds C(4)–C(5) and C(2)–C(3) are slightly rotated (by 5.2°) relative to each other, and the thiocyanate group is in an approximately coplanar *s-trans* orientation to C(4)–C(5), torsion angle C(4)–C(5)–S(1)–C(11) = –176.7°. This points to an insignificant steric influence of the geminal methyl group in contrast to the vicinal one. α,β -unsaturated esters are found to exist as a mixture of the *s-cis* and *s-trans* forms on the basis of their lanthanide-induced shift (LIS) spectra (Montando, Librando, Caccamese & Marvigna, 1973). Brunn, Dethloff & Riebenstahl (1977) have discussed the IR and UV spectra of α,β -unsaturated esters and assumed in nonpolar solutions the *s-trans-s-trans* conformation. In polar solutions, however, *s-cis-s-trans* conformations have been taken into account. We have found that in CMTHCE, of the possible stereoisomeric forms of the ester group with reference to the C(2)–C(3) double bond, a planar *s-cis-s-trans* conformation occurs [torsion angle C(3)–C(2)–C(1)–O(1) = 2.7°].

References

- ALEXANDER, E. R. & COPE, A. C. (1944). *J. Am. Chem. Soc.* **66**, 886–888.
- ASTLE, M. J. & ZASLOWSKY, J. A. (1952). *Ind. Eng. Chem.* **44**, 2867–2869.
- BAKER, W. & HOWES, C. S. (1953). *J. Chem. Soc.* pp. 119–124.
- BRUNN, J., DETHLOFF, M. & RIEBENSTAHL, H. (1977). *Z. Phys. Chem. (Leipzig)*, **258**, 209–218.
- CAWLEY, C. M., EVANS, J. T. & FARMER, E. H. (1930). *J. Chem. Soc.* pp. 522–530.
- CERNAYOVA, M., KOVAC, J., DANDAROVA, M. & RAJNIAKOVA, O. (1977). *Collect. Czech. Chem. Commun.* **42**, 347–352.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- HAYASHI, T. (1966). *J. Org. Chem.* **31**, 3252–3258.
- HAYASHI, T., IGARASHI, M., HAYASHI, S. & MIDORIKAVA, H. (1965). *Bull. Chem. Soc. Jpn.*, **38**, 2063–2067.
- HERZSCHUH, R., SCHULZE, B. & MÜHLSTÄDT, M. (1981). In preparation.
- JOHNSON, C. K. (1965). *ORTEP*. Rep. ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN-78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
- MASTAGLI, P., LAMBERT, P. & ANDRIC, N. (1956). *Bull. Soc. Chim. Fr.* **23**, 796–798.
- MONTANDO, G., LIBRANDO, V., CACCAMESE, S. & MARVIGNA, P. (1973). *J. Am. Chem. Soc.* **95**, 6365–6370.
- MÜHLSTÄDT, M., BRÄMER, R. & SCHULZE, B. (1976). *Z. Chem.* **16**, 49–51.
- POPP, F. D. & CATALA, A. (1961). *J. Org. Chem.* **26**, 2738–2740.
- SCHULZE, B., BRÄMER, R., KLEINPETER, E. & MÜHLSTÄDT, M. (1976). *J. Prakt. Chem.* **318**, 795–800.
- SCHULZE, B., MÜHLSTÄDT, M., BALDAUF, C. & BRÄMER, R. (1977). *Z. Chem.* **17**, 367–368.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1976). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.