The Crystal and Molecular Structure of Ethyl m-Nitroso-
trans-cinnamate

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The crystal and molecular structure of ethyl m-
nitroso-trans-cinnamate, C_{11}H_{11}O_{3}N, has been
determined from X-ray diffraction data collected at
−165 °C and refined by least squares methods. The
space group is P2_1/n with cell dimensions
a = 12.065(4) Å, b = 15.626(3) Å, c = 5.387(2) Å and
β = 92.44(2)° at −165 °C. The final R factor was
5.4% and the estimated standard deviations in bond
lengths involving only non-hydrogen atoms ranged
from 0.003 to 0.005 Å. The C–NO bond length
(1.451 Å) is longer and the N–O bond length
(1.229 Å) probably shorter in this molecule than in
any previously studied nitrobenzene. Other bond
lengths and angles are very similar to those of
cinnamic acid and some of its derivatives. The
molecule is essentially planar.

The present structure investigation of ethyl m-
nitroso-trans-cinnamate (I) is part of a series of
investigations of C-nitroso compounds. The earlier
parts of this series have been devoted to nitroso-
benzenes shown to have molecular structures
consistent with substantial mutual conjugation
between an oxide, 1, 2 a dialkylamino, 3, 4 and a
hydroxyl 5 group and the nitroso group. Absence
of mutual conjugation in the title compound makes
it a reference substance to the molecules previously
investigated.

An X-ray investigation has shown that the natural
reference compound, nitrobenzene, exists in an
azo dioxime dimeric state in its stable crystals. 6 This
seems to be the case also for all other potential
reference molecules studied. The azo dioxime
dimeric state is indicated by IR spectroscopy or solely by
absence of colour in these cases (Ref. 7 and
references therein). Interestingly, dealkylation of (I)
gives an acid forming very stable colourless crystals
whereas only green coloured crystals have so far
been found for the title compound.

EXPERIMENTAL

The title compound was derived from the cor-
responding nitro compound by use of a standard
method. 4 Using a somewhat modified method
described by Mijis et al. 9 only the corresponding
azoxy compound could be isolated (golden coloured,
m.p. 90 °C, IR-KBr bands at 1455 and 1300
cm⁻¹). Monomeric ethyl m-nitroso-trans-cinnamate
crystallizes in two forms. The one investigated (α)
collected in the condenser and separated from the
distillate upon steam distillation. The β form sepa-
rated from the filtrated reaction mixture over a
period of a week in the refrigerator. The light
green and crisp needle-shaped β crystals melt at
55 °C. They have monoclinic symmetry, a needle
axis of 4.02 Å, a unique axis of 15.36 Å and a some-
what smaller unit cell volume (1015 Å³) than the α
crystals. The IR-KBr band is at 1480 cm⁻¹.
Sublimation by use of a cold finger gave reformation
of the β form. Also subsequent evaporation of a
diethyl ether solution resulted in β crystals.
Continuous recrystallization from diethyl ether, however,
gave increasing amounts of the α form. Crystals
suited for the diffactometer measurements could not
be found. The emerald-coloured elongated tabular
α crystals melt at 65 °C. In contrast to the β crystals
they are plastic. The α crystal used for the diffractom-
eter measurements was grown from a melt. This
was accomplished by carefully melting α crystals
until near completion followed by controlled re-
crystallization on a “THERMOPAN” melting
point apparatus. The crystal was perfectly shaped
and of dimensions 0.44 × 0.16 × 0.08 mm. Apart
from the following details the experimental condi-
tions in connection with the diffractometer measure-
ments were as those described in Ref. 3. The tempera-
ture at the crystal site was −165 °C. The scan limits
were 2θ(α₁) = 1.1° and 2θ(α₂) + 1.1° and a quadrant
of reciprocal space was examined. Reflections up
to 65° in 2θ were measured; below 40° all, above
40° those having integrated counts larger than a
preset value during a 2s scan over the peak. Out of 2151 unique reflections measured 1303 had intensities larger than 2.5σ(I) where σ(I) is the standard deviation of the intensity based on counting statistics adding 2% uncertainty due to experimental fluctuations. The atomic scattering factors for the heavy atoms were those of Doyle and Turner and for hydrogen those of Stewart et al. All programs except for the ORTEP program (Ref. 11 in Ref. 3) and the MULTAN program (Ref. 12 in Ref. 3) applied during the investigation are described in Ref. 12.

CRYSTAL DATA

Ethyl m-nitroso-trans-cinnamate or trans-3-(3-nitrosophenyl)propenoic acid ethyl ester, C₁₁H₁₂O₃N, monoclinic α form, space group P2₁/n (No. 14). Dimensions of the unit cell at −165 °C: a = 12.065(4) Å, b = 15.626(3) Å, c = 5.387(2) Å and β = 92.44(2)°; V = 1014.7 Å³. At 18 °C (film): a = 12.99 Å, b = 15.83 Å, c = 5.46 Å, β = 103°; V = 1115 Å³. M = 205.22, F(000) = 432, Dcak(18 °C) = 1.22 g cm⁻³, Dcak(−165 °C) = 1.343 g cm⁻³, Z = 4.

STRUCTURE DETERMINATION

The structure was determined by direct methods (MULTAN) and refined by full matrix least squares techniques. Initial positional parameters for hydrogen atoms were obtained from a ΔF synthesis. The refinement including all atoms and all observed reflections converged with R = 0.054, a weighted R_w factor of 0.043 and a goodness of fit S of 1.6. A list of structure amplitudes is available from the author. Final parameters from the refinement with all the observed reflections are given in Table 1. Magnitudes and directions of the principal axes of the vibrational ellipsoids are indicated in Fig. 1. A rigid body analysis of the entire molecule shows a fairly good agreement between observed and calculated vibration tensor elements (ΔU_m = 0.0030 Å²). The agreement is slightly better for the nitroso-phenyl moiety (ΔU_m = 0.0025 Å²). For the entire molecule the r.m.s. eigenvalues of T are 0.15, 0.14

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factors are expressed as: exp [−2π²(h²a*²U₁₁ + ⋯ + 2kb*c*U₂₃)]. Estimated standard deviations in parentheses.

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<td>O11—C1—O12</td>
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<td>C2—C3—C4</td>
<td>127.3(3)</td>
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<td>C3—C4—C5</td>
<td>118.3(3)</td>
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<td>C3—C4—C9</td>
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<td>C4—C5—C6</td>
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<td>C5—C6—C7</td>
<td>121.1(3)</td>
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<tr>
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<tr>
<td>C10—O11—C1</td>
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<td>C7—C8—C9</td>
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<tr>
<td>C1—C2—C3</td>
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<td>C9—C4—C5</td>
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Inter-molecular contacts

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<tbody>
<tr>
<td>O11···N6(a)</td>
<td>3.282</td>
<td>N6···C10(c)</td>
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<tr>
<td>O6···C10(b)</td>
<td>3.225</td>
<td>O12···C3(b)</td>
<td>3.306</td>
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<tr>
<td>O6···C1(a)</td>
<td>3.372</td>
<td>O12···C5(b)</td>
<td>3.333</td>
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Torsion angles

<table>
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<th>Torsion angles</th>
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</thead>
<tbody>
<tr>
<td>O6—N6—C6—C5</td>
<td>0.7(5)</td>
<td>O12—C1—C2—C3</td>
<td>-4.6(5)</td>
</tr>
<tr>
<td>C11—C10—O11—C1</td>
<td>-178.6(3)</td>
<td>C2—C3—C4—C9</td>
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<tr>
<td>C10—O11—C1—O12</td>
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</table>

Symmetry code

(a): x + 3/2, y + 1/2, -z + 1, (b): -x + 2, -y + 1, -z + 1, (c): -x + 1, -y + 1, -z + 1

and 0.13 Å, and of L 3.7, 1.4 and 0.8°, corresponding to librational bond lengthenings in the range 0.001 – 0.003 Å. The estimated standard deviations (e.s.d.’s) were derived from the final correlation matrix of the least squares refinement. The C–H bond lengths are in the range 0.90 – 1.07 Å with e.s.d.’s of 0.03 Å. Other bond lengths and angles involving non-hydrogen atoms are given in Table 2.

**DISCUSSION**

The crystal structure is similar to that of the related methyl p-hydroxy-m-nitro-trans-cinnamate, (II). Characteristic for both is the infinite layers of edge-to-edge packed molecules close to (101) planes and the existence of several nearly linear *intra*-layer CH–O(N) contacts which stabilize the sheet-like arrangement of molecules. The nitroso oxygen atom, however, is only participating in non-linear and loose H-contacts (above 2.66 Å). The COOEt group has one *intra*-layer neighbouring NO group and is sandwiched by two nitroso groups. These structural features are illustrated in Fig. 2 which also reveals nearly "close" packing normal to the (10 – 3) plane. A C3···C3’ contact of 3.387 Å (3.295 Å from the benzene ring plane) and a C3···C8 contact of 3.391 Å are the only C–C *inter*-layer contacts shorter than 3.65 Å. The lack of extensive *inter*-molecular π–π overlapping apparently makes the present structure rather loose (packing coefficient of 0.76) and may explain the drastic change in a and β when the temperature is increased to 18 °C. These changes seem to involve a considerable (0.4 Å) increase in the *inter*-molecular spacing, indicating a starting-up of coordinated flipping of the stacked terminal groups. The latter is

consistent with the plastic character of the crystal at 18 °C.

The molecular structure. The ethyl ester of m-nitrosob-trans-cinnamic acid (I) conforms with most other alkyl cinnamates and cinnamic acids in having three nearly coplanar parts each being planar within the accuracy of the experiment. In the present case the three parts are the phenyl ring with N6 and C3, the four-atom olefinic group and the CCOOC fragment. More details are given in Table 3. The molecule as a whole is also essentially planar as the twist about the O—CH₂ and the C—NO bond is less than 1.5°. In agreement with all other trans alkyl cinnamates the conformation about the C—OEt and the C—COOEt bond is, respectively, anti (the R groups are anti) and syn. The anti C₆₅,—C conformation, however, makes (I) a unique meta substituted cinnamate.

Owing to different libration effects it is difficult to compare directly the bond lengths with those of (II), p-methoxycinnamic acid (III) and of cinnamic acid (IV). Otherwise, however, such a comparison seems appropriate as judged from the experimental technique used, the R factors, the e.s.d.’s and the resolution achieved. If one excludes the C—O bonds in the acids there are only six significant differences between bond lengths in (I) and corresponding ones in the other molecules (in the range 0.013—0.025 Å). Three involve distances in the side chain as compared to (II) and may possibly be ascribed to libration effects. The others conform with expected conjugation involving the para substituents. The average ring bond length is the same within 0.001 Å for all four molecules. Using reasonably enlarged e.s.d.’s (by a factor √2) a χ² test gives a probability of 0.5 for the ring bond lengths being randomly distributed about the mean value [1.387(6) Å] in (I). Although of limited value, this gives reason for not discussing in detail the spread in the ring bond lengths. The latter is actually smaller than in cinnamic acid (probably due to

---

**Table 3.** Deviation (Å) of atoms from least squares planes. Atoms defining the planes are marked with an asterisk.

<table>
<thead>
<tr>
<th>Atom/Plane</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>O11</td>
<td>0.052</td>
<td>-0.007*</td>
<td>0.000*</td>
</tr>
<tr>
<td>O12</td>
<td>0.159</td>
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<tr>
<td>O6</td>
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<tr>
<td>N6</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>0.100</td>
<td>-0.007*</td>
<td>0.000*</td>
</tr>
<tr>
<td>C2</td>
<td>0.068</td>
<td>0.006*</td>
<td>0.000*</td>
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<tr>
<td>C3</td>
<td>0.013</td>
<td>0.009*</td>
<td>0.094</td>
</tr>
<tr>
<td>C4</td>
<td>0.003*</td>
<td>-0.008*</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>-0.003*</td>
<td>-0.056</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>0.003*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>-0.002*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>0.002*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C9</td>
<td>-0.003*</td>
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<tr>
<td>C11</td>
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<td>-0.027</td>
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</tbody>
</table>

**Inter-planar angles:** AB, 2.7°; BC, 4.6°; AC, 1.9°

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liberation effects). In consistency with the finding of an essentially unperturbed benzene ring the C—NO bond length ($R_{CN} = 1.451(4)$ Å) is close to that usually accepted for a “pure” $C(sp^2) - N(sp^2)$ single bond (1.458 Å).\textsuperscript{16} Comparison with 5-nitrososalicylic acid (V) shows that $R_{CN}$ is 0.025 Å longer and that the N—O bond length [$R_{NO} = 1.229(3)$ Å] is 0.005 Å shorter in (I) than in (V). Although the latter difference is rather uncertain (e.s.d. of 0.004 Å) it seems reasonable on the basis of a previously found relationship between $R_{NO}$ and $R_{CN}$.\textsuperscript{2} Using this relationship a regression of 0.010 Å (to 1.223 Å) is obtained for $R_{NO}$ upon changing $R_{CN}$ from 1.426 Å [as in (V)] to 1.451 Å. The nitrogen bond angle [113.5(3)°] is smaller than in any of the other nitrosobenzenes. This strengthens an earlier assumption concerning the connection between $\angle CNO$ and the conjugation over the C—N—O group.\textsuperscript{2,5} In short it may be stated that the geometry of the nitroso group in (I) is consistent with a smaller charge displacement to the group than in any other nitrosobenzene investigated.

REFERENCES


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