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, $C_{11}H_{11}O_3N$, 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 $a=12.065(4)\text{ \AA}$, $b=15.626(3)\text{ \AA}$, $c=5.387(2)\text{ \AA}$ and $\beta=92.44(2)^\circ$ 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 $\text{\AA}$. The C–NO bond length (1.451 $\text{\AA}$) is longer and the N–O bond length (1.229 $\text{\AA}$) probably shorter in this molecule than in any previously studied nitrosobenzene. 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 nitrosobenzenes shown to have molecular structures consistent with substantial mutual conjugation between an oxide,^{1,2} a dialkylamino^{3,4} and a hydroxyl⁵ 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, nitrosobenzene, exists in an azo dioxide dimeric state in its stable crystals.⁶ This seems to be the case also for *all* other potential reference molecules studied. The azo dioxide 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 corresponding nitro compound by use of a standard method.⁸ Using a somewhat modified method described by Mijs *et al.*⁹ only the corresponding azoxy compound could be isolated (golden coloured, m.p. 90°C , IR-KBr- ω_{NNO} 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 separated 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 $\text{\AA}$, a unique axis of 15.36 $\text{\AA}$ and a somewhat smaller unit cell volume (1015 $\text{\AA}^3$) than the α crystals. The IR-KBr- ω_{NO} 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. Continued recrystallization from diethyl ether, however, gave increasing amounts of the α form. Crystals suited for diffractometer 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 diffractometer measurements was grown from a melt. This was accomplished by carefully melting α crystals until near completion followed by controlled recrystallization on a "THERMOPAN" melting point apparatus. The crystal was perfectly shaped and of dimensions $0.44 \times 0.16 \times 0.08\text{ mm}$. Apart from the following details the experimental conditions in connection with the diffractometer measurements were as those described in Ref. 3. The temperature at the crystal site was -165°C . The scan limits were $2\theta(\alpha_1) - 1.1^\circ$ and $2\theta(\alpha_2) + 1.1^\circ$ 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 $2.5\sigma(I)$ where $\sigma(I)$ 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 Turner¹⁰ and for hydrogen those of Stewart *et al.*¹¹ 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, $C_{11}H_{11}O_3N$, monoclinic α form, space group $P2_1/n$ (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 $\beta = 92.44(2)^\circ$; $V = 1014.7$ Å³. At 18°C (film): $a = 12.99$ Å, $b = 15.83$ Å, $c = 5.46$ Å, $\beta = 103^\circ$; $V = 1115$ Å³. $M = 205.22$, $F(000) = 432$, $D_{\text{calc}}(18^\circ\text{C}) = 1.22$ g cm⁻³, $D_{\text{calc}}(-165^\circ\text{C}) = 1.343$ g cm⁻³, $Z = 4$.

STRUCTURE DETERMINATION

The structure was determined by direct methods (MULTAN) and refined by full matrix least squares techniques.¹² 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

Fig. 1. 50 % probability ellipsoids and numbering of atoms.

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 ($\Delta U_{\text{rms}} = 0.0030$ Å²). The agreement is slightly better for the nitroso-phenyl moiety ($\Delta U_{\text{rms}} = 0.0025$ 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: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. Estimated standard deviations in parentheses.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O11	.46517(19)	.25993(12)	.81444(44)	.0301(13)	.0166(11)	.0241(13)	.0030(9)	-.0055(10)	.0007(9)
O12	.49370(19)	.37636(13)	1.02970(44)	.0390(14)	.0191(11)	.0250(14)	-.0029(11)	-.0049(11)	.0024(11)
O6	.31016(21)	.70870(14)	.52102(46)	.0498(16)	.0267(13)	.0377(16)	.0030(12)	.0019(13)	.0004(13)
N6	.26099(23)	.75634(16)	.33550(57)	.0300(16)	.0272(17)	.0320(18)	.0022(13)	.0001(15)	.0074(15)
C1	.45108(26)	.34198(19)	.80061(66)	.0268(20)	.0150(15)	.0261(21)	.0010(14)	.0059(17)	.0018(16)
C2	.36912(26)	.38448(20)	.64470(62)	.0239(20)	.0196(16)	.0220(19)	.0016(14)	-.0006(16)	.0025(15)
C3	.38329(25)	.46905(20)	.64030(60)	.0225(20)	.0230(18)	.0150(18)	.0014(14)	.0003(16)	.0034(15)
C4	.32361(24)	.52348(18)	.45400(58)	.0176(17)	.0190(15)	.0186(18)	.0002(13)	.0029(14)	.0039(14)
C5	.32420(26)	.61107(19)	.48085(62)	.0195(19)	.0224(17)	.0182(19)	.0012(14)	.0001(15)	.0019(14)
C6	.26782(27)	.66363(19)	.31782(59)	.0210(20)	.0185(16)	.0224(22)	.0042(13)	.0019(16)	.0012(14)
C7	.21197(27)	.62967(21)	.11109(67)	.0239(19)	.0205(19)	.0216(19)	.0060(16)	.0012(15)	.0102(16)
C8	.21123(29)	.64108(21)	.07612(66)	.0266(21)	.0271(18)	.0217(19)	.0001(15)	.0003(16)	.0055(16)
C9	.26714(26)	.48950(20)	.24503(65)	.0243(19)	.0221(17)	.0225(17)	.0013(14)	.0041(15)	.0031(16)
C10	.31557(29)	.20099(20)	1.00073(67)	.0266(20)	.0183(16)	.0260(19)	.0002(16)	-.0022(16)	.0045(17)
C11	.50927(33)	.11556(21)	.94220(80)	.0332(21)	.0180(19)	.0309(25)	.0004(17)	-.0027(19)	.0030(17)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H2	.354(2)	.349(2)	.621(5)	1.0(6)	H3	.422(2)	.500(2)	.763(5)	.7(6)
H5	.362(2)	.634(2)	.676(5)	.8(6)	H7	.174(2)	.666(2)	.006(6)	.1(6)
H8	.160(2)	.516(2)	-.069(6)	2.9(8)	H9	.264(2)	.420(2)	.211(5)	.9(6)
H10	.594(2)	.231(2)	1.022(5)	1.2(6)	H102	.406(2)	.225(2)	1.167(6)	2.0(8)
H11	.554(2)	.084(2)	1.009(6)	2.0(7)	H112	.542(3)	.103(2)	.764(7)	5.4(10)
H113	.433(3)	.094(2)	.950(6)	2.9(8)					

Table 2. Bond lengths (Å) and angles (°).

Bond lengths			
O6–N6	1.229(3)	C4–C5	1.391(4)
O11–C1	1.360(3)	C5–C6	1.388(4)
O12–C1	1.201(4)	C6–C7	1.385(4)
O11–C10	1.449(4)	C7–C8	1.385(4)
N6–C6	1.451(4)	C8–C9	1.378(5)
C1–C2	1.470(5)	C9–C4	1.396(4)
C2–C3	1.333(4)	C10–C11	1.505(5)
C3–C4	1.474(4)		
Bond angles			
O11–C1–O12	122.7(3)	C2–C3–C4	127.3(3)
O11–C1–C2	111.1(3)	C3–C4–C5	118.3(3)
O12–C1–C2	126.2(3)	C3–C4–C9	122.7(3)
O6–N6–C6	113.5(3)	C4–C5–C6	119.5(3)
N6–C6–C5	124.6(3)	C5–C6–C7	121.1(3)
N6–C6–C7	114.2(3)	C6–C7–C8	119.4(4)
C10–O11–C1	114.7(3)	C7–C8–C9	120.0(4)
C11–C10–O11	107.5(3)	C8–C9–C4	121.0(3)
C1–C2–C3	119.3(3)	C9–C4–C5	119.0(3)
Inter-molecular contacts			
O11...N6(a)	3.282	N6...C10(c)	3.379
O6...C10(b)	3.225	O12...C3(b)	3.306
O6...C1(a)	3.372	O12...C5(b)	3.333
Torsion angles			
O6–N6–C6–C5	0.7(5)	O12–C1–C2–C3	–4.6(5)
C11–C10–O11–C1	–178.6(3)	C2–C3–C4–C9	2.7(5)
C10–O11–C1–O12	0.3(4)		
Symmetry code			
(a): $-x+3/2, y+\frac{1}{2}, -z+\frac{1}{2}$, (b): $-x+2, -y+1, -z+1$, (c): $-x+1, -y+1, -z+1$			

and 0.13 Å, and of $\angle$ 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).¹³ Characteristic for both is the infinite layers of edge-to-edge packed molecules close to (10) planes and the existence of several nearly linear *intra*-layer CH...O(N) contacts which stabilize the sheet-like arrangement of molecules.¹³ 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

Fig. 2. A stereoscopic illustration of the structure.

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

The molecular structure. The ethyl ester of *m*-nitroso-*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.¹⁴ 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*.^{13–15} The *anti* C_{Ar}–C conformation, however, makes (I) a unique *meta* substituted cinnamate.^{13–15}

Owing to different libration effects it is difficult to compare directly the bond lengths with those of (II), *p*-methoxycinnamic acid (III)¹⁴ and of cinnamic acid (IV).¹⁴ 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 $\sqrt{2}$) a χ^2 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.

Atom/Plane	A	B	C
O11	0.052		0.000*
O12	0.159	–0.092	0.000*
O6	0.030		
N6	0.013		
C1	0.100	–0.007*	0.000*
C2	0.068	0.006*	0.000*
C3	0.013	0.009*	0.094
C4	0.003*	–0.008*	
C5	–0.003*	–0.056	
C6	0.003*		
C7	–0.002*		
C8	0.002*		
C9	–0.003*		
C10	0.071		0.008
C11	0.047		–0.027

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

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

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