X-Ray Investigation of Methyl *m*-Azoxy-*trans*-cinnamate

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In an attempt to derive methyl *m*-nitrosocinnamate from the corresponding nitro compound by use of a standard method[1] golden coloured crystals melting at 175 °C were obtained. The present X-ray structure analysis at −165 °C has shown this compound to be methyl *m*-azoxy-*trans*-cinnamate. The crystals formed upon slow evaporation of an acetone solution of a sample purified by sublimation. Film investigation at room temperature showed monoclinic symmetry and unit cell dimensions deviating less than 3 % from those at low temperature. The diffractometer measurements were done using a prismatic crystal of dimensions $0.57 \times 0.12 \times 0.04$ mm. High crystal perfection prevented overlap between the reflections: $(\Delta 2\theta)_{min} = 1.07°$ along c^* (Mo$K\alpha$ radiation). The scan width was $[2\theta(\alpha_1) - 0.6] - [2\theta(\alpha_2) + 0.6]°$. Within a quadrant of reciprocal space and with $2\theta_{max} = 70°$, 1847 reflections were measured; 1231 had intensities larger than $2.5\sigma(I)$ and were used in the further work. Other details in connection with the data collection, the data treatment, the atomic scattering factors and the computer programs used may be found in publications devoted to studies of *C*-nitroso compounds performed in this laboratory.[2] The crystal data for methyl *m*-azoxy-*trans*-cinnamate at −165 °C are: $C_{20}H_{18}O_5N_2$, monolinic, space group $P2_1/c$, $a = 3.8251(8)$ Å, $b = 5.825(1)$ Å, $c = 38.364(7)$ Å, $\beta = 90.73(2)°$, $V = 854.7$ Å^3, $M = 366.38$, $Z = 2$, $D_{calc} = 1.424$ g cm^{-3}, $F(000) = 384$.

An approximate and centrosymmetrical structural model was obtained by use of the MULTAN program package. Fully ordered it is that of methyl *m*-nitroso-*trans*-cinnamate in an azo dioxide dimeric state, *i.e.* an *N*-oxide derivative of the title compound. Including hydrogen atoms (from ΔF-maps) and with anisotropic temperature factors for the heavy atoms this model was refined to a conventional *R*-factor of 0.11 (full matrix least-squares refinement). Then all structural results but the B_{11} value for the nitroso oxygen atom (O6) appeared reasonable. Introduction of half occupancy at the O6 site and subsequent refinement yielded a lowering of *R* to 0.059. This, in connection with the finding by MS of $M = 366$, showed that the compound under investigation was actually the title compound. The best model then consists of two half azoxy molecules superimposed so that all atoms apart from the O6 atom coincide. The final weighted R_w and goodness of fit *S* were 0.047 and 1.67, respectively. The parameter values at convergence are listed in Table 1. For bond lengths involving only heavy atoms the estimated standard deviations range from 0.003 to 0.005 Å. Bond

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factors are expressed as: $\exp[-(B_{11}h^2 + \cdots + B_{23}kl)]$. Estimated standard deviations in parentheses.

ATOM	x	y	z	B11	B22	B33	B12	B13	B23
O11	0.6416(5)	0.9529(4)	0.18419(4)	0.068(2)	0.0252(8)	0.00025(1)	-0.009(2)	0.0009(2)	-0.0003(2)
O12	0.8513(5)	0.6350(4)	0.21055(4)	0.084(2)	0.0335(9)	0.00023(1)	-0.007(2)	-0.0016(3)	0.0018(2)
O6	0.7238(10)	0.7163(6)	0.02021(8)	0.060(3)	0.0170(13)	0.00031(3)	0.034(3)	0.0005(4)	-0.0005(3)
N6	0.9469(6)	0.5290(4)	0.01482(5)	0.051(2)	0.0253(9)	0.00045(2)	-0.026(2)	0.0035(3)	-0.0038(2)
C1	0.7844(7)	0.7434(5)	0.18450(7)	0.041(2)	0.0252(12)	0.00029(2)	-0.025(3)	-0.0002(3)	-0.0001(2)
C2	0.8528(7)	0.6661(5)	0.14850(6)	0.041(2)	0.0198(10)	0.00027(2)	-0.007(2)	-0.0003(3)	0.0009(2)
C3	1.0022(7)	0.4665(5)	0.14168(7)	0.037(2)	0.0219(11)	0.00033(2)	-0.013(3)	-0.0012(3)	0.0027(2)
C4	1.0782(6)	0.3715(5)	0.10724(7)	0.021(2)	0.0120(9)	0.00051(2)	-0.005(2)	-0.0001(3)	0.0007(2)
C5	0.9883(7)	0.4846(5)	0.07647(7)	0.029(2)	0.0099(9)	0.00041(2)	-0.001(2)	0.0010(3)	-0.0005(2)
C6	1.0630(7)	0.3899(5)	0.04423(7)	0.036(2)	0.0196(10)	0.00041(2)	-0.018(2)	0.0015(3)	-0.0014(2)
C7	1.2213(8)	0.1764(6)	0.04239(11)	0.037(3)	0.0260(14)	0.00105(4)	-0.017(3)	0.0044(5)	-0.0072(4)
C8	1.3090(8)	0.0621(6)	0.07284(13)	0.031(2)	0.0128(11)	0.00167(5)	0.005(3)	0.0004(5)	-0.0034(4)
C9	1.2407(8)	0.1590(5)	0.10467(10)	0.032(2)	0.0134(10)	0.00101(3)	-0.007(2)	-0.0012(4)	0.0019(3)
C10	0.5550(10)	1.0466(7)	0.21854(8)	0.069(3)	0.0340(15)	0.00028(2)	-0.013(4)	0.0007(4)	-0.0017(3)

ATOM	x	y	z	B	ATOM	x	y	z	B
H2	0.776(6)	0.759(4)	0.1302(6)	2.0(6)	H3	1.063(7)	0.379(5)	0.1611(6)	2.9(6)
H5	0.872(6)	0.623(4)	0.0768(6)	2.0(6)	H7	1.267(9)	0.112(6)	0.0223(8)	5.3(9)
H8	1.429(9)	-0.082(6)	0.0712(8)	6.0(9)	H9	1.303(8)	0.082(5)	0.1255(7)	3.9(7)
H101	0.382(8)	0.948(5)	0.2280(7)	3.8(8)	H102	0.769(8)	1.052(5)	0.2333(7)	3.6(7)
H103	0.464(9)	1.203(6)	0.2125(7)	5.3(9)					

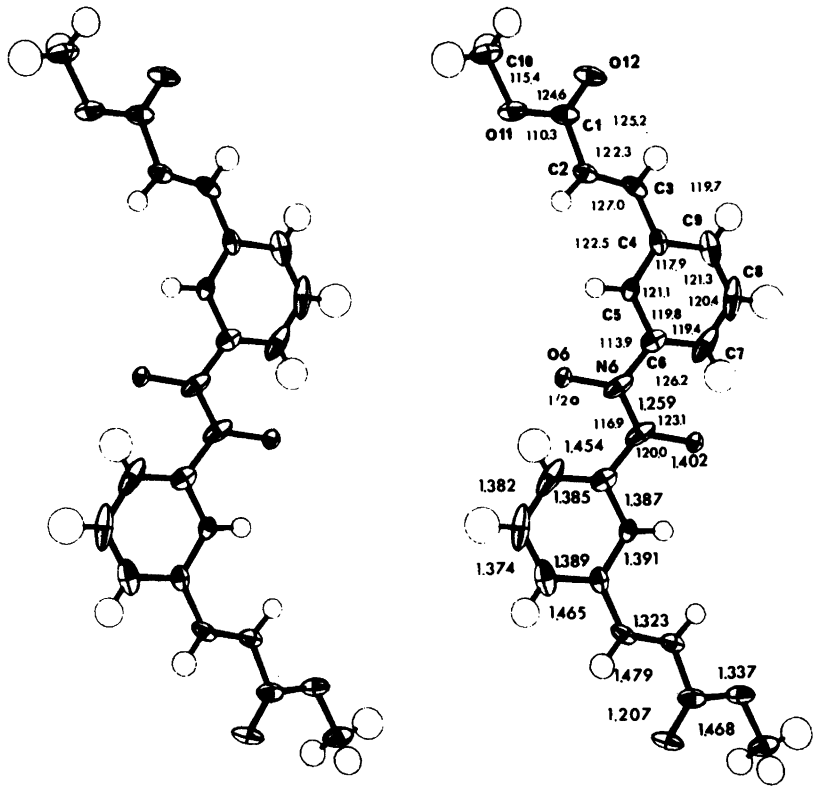

Fig. 1. Bond lengths (Å), bond angles (°), numbering of atoms and 50 % probability ellipsoids. The projection of the *c* axis intersects the C8 – H and the O11 – C10 bond midway while the *a* axis is normal to the paper plane.

lengths, angles and other structural results are given in Fig. 1.

The packing pattern is similar to those for smectogenic compounds in that the molecules are arranged in layers having carbomethoxy boundaries. However, the title compound seems not to have a smectic mesophase (countrary to its *para* analogue). This may probably be due to the fact that the molecules are close-packed rather than stacked within these layers.[3]

Apparently the disorder determines to a large extent the shape of the probability ellipsoids of all atoms but the O6 atom. In the azoxy group the structural results indicate the NO nitrogen atom to reside in the ring-far half of the N6 ellipsoid. The average CNONC fragment is planar and inclined 12.3° to the planar benzene ring. This conformation is somewhat different from that of the smectogenic and nearly planar ethyl *p*-azoxybenzoate.[3]

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