The Crystal Structures of 2-Bromo-1-methyl-benzo[c]-pyrazolo[1:2-a]pyrazole-3:9-dione and 3-Bromo-2-methyl-pyrazolo[a][3,1]benzoxazin-5-one

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The structures of monobromo-derivatives of the so-called α- and β-pyrazoisocoumarazone isomers, $C_{11}H_7N_2O_2Br$, have been confirmed by three-dimensional X-ray diffraction crystal structure analyses as being 2-bromo-1-methyl-benzo[c]pyrazolo[1:2-a]pyrazole-3:9-dione and 3-bromo-2-methyl-pyrazolo[a][3,1]benzoxazin-5-one, respectively.

Crystals of the α-derivative are monoclinic, with unit cell dimensions $a = 19.51 \pm 0.05$ Å, $b = 9.13 \pm 0.05$ Å, $c = 13.96 \pm 0.05$ Å, $\beta = 118.0 \pm 0.5°$ and space group $C2/c$, while β-derivative crystals, also monoclinic, have $a = 5.45 \pm 0.01$ Å, $b = 14.78 \pm 0.01$ Å, $c = 12.73 \pm 0.01$ Å, $\beta = 90.7 \pm 0.1°$ and space group $P2_1/n$.

Because crystals of the α-compound were extremely small and difficult to prepare, the diffraction data set consisted of only 261 photographically-determined, independent, non-zero reflections ($2\theta_{max} = 37°$ for CuKα). However, 1112 diffractometer-measured intensities were used in the analysis of the β-isomer. Both crystal structures were solved from successive three-dimensional Fourier maps following the initial placement of the bromine atoms from Patterson syntheses. Full matrix least squares refinement of the complete structure postulates reduced the usual R to 0.175 for the α-derivative and 0.074 for the β-compound.

Molecules of both derivatives are approximately planar and their packing in both crystal structures is determined by van der Waals forces, the shortest contact distances being from bromine atoms to oxygens of neighbouring molecules.

This paper describes the crystal structures of monobromo-derivatives of Michaelis's methyl-pyrazoisocoumarazones, and their analyses from three-dimensional X-ray diffraction data.

After condensation of o-carboxyphenylhydrazine with ethylacetoacetate and then distillation of the resulting o-carboxyphenylhydrazone, Michaelis et al.[1,2] isolated what were reported to be three isomeric heterocyclic products, which were called α-, β-, and γ-methyl-pyrazoisocoumarazone, respectively.

Much later Veibel *et al.*[3-6] showed that Michaelis's γ-isomer was actually a 1:2 mixture of the α- and β-compounds, and also proved that both the α- and the β-modifications yield the same pyrazolone ester when titrated in ethanol with standard base. From the method of preparation, the titration results and the dipole moments of the compounds they concluded that, of the formulae proposed by Michaelis, the β-modification might have structure II, but that there was some doubt that the α-modification had structure I. However, Mosby[7] found nothing inconsistent with this assignment of structures in the results of an infrared spectral investigation.

I   II
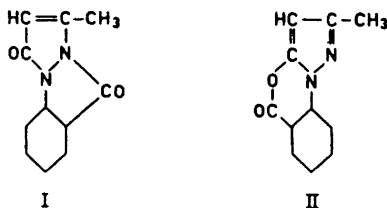
Further study of these and analogous compounds is being pursued by Else Plejl, Department of Organic Chemistry, Technical University of Denmark, who suggested the X-ray crystallographic analyses to resolve the structural ambiguities and who kindly provided crystals of the monobromo-derivatives of α- and β-"methyl-pyrazoisocoumarazone".

α-Compound   β-Compound
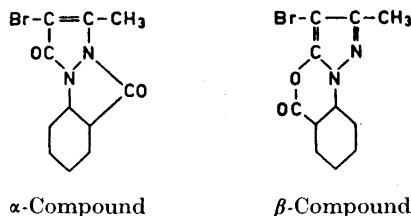
EXPERIMENTAL

Recrystallization. Single crystals of the α-*derivative* were obtained by evaporation of a 96 % ethanol solution at 1°C. Their melting point was 187 ± 1°C. They were very small, poorly-formed, colourless plates. None could be grown with characteristics suitable for diffractometer data measurement.

This was not the case for the β-*derivative*, however, suitable crystals being deposited by slowly decreasing the temperature of a 96 % ethanol solution from 10°C to 2°C. These formed as somewhat elongated, colourless prisms with melting point 148 ± 1°C.

X-Ray diffraction data collection and measurement. (1) *The α-derivative.* A single crystal of dimensions $0.15 \times 0.05 \times 0.005$ mm³ was mounted on a Weissenberg goniometer with its *b* axis (see Crystal Data) parallel to the rotation axis. Space group and approximate unit cell dimensions were determined from preliminary oscillation and Weissenberg photographs. More accurate unit cell dimensions were later determined from a powder diagram taken with Cu$K\alpha$ radiation. Three-dimensional, multiple-film, equi-inclination Weissenberg photographs were taken for layers 0 to 4, inclusive, with

rotation axis b, using Cu$K\alpha$ radiation. The diffracted intensities for each layer were measured visually, scaled together and then corrected for Lorentz and polarization effects. The size and shape of the crystal did not allow data collection about a second axis, and so the layers of b-axis data were scaled together on the basis of their relative exposure times. Absorption corrections were not applied. Intensities above background were observed only to a 2θ of 37° so that the final data set consisted of 261 independent, non-zero structure amplitudes.

(2) *The β-derivative.* Unit cell dimensions were measured from precession photographs taken with Mo$K\alpha$ radiation of a single crystal of dimensions $0.10 \times 0.11 \times 0.14$ mm³ which had its a axis (see Crystal Data) parallel to the goniometer head axis. This crystal was also used to measure and collect a three-dimensional set of diffracted intensities, being mounted for the purpose on a Stoe automatic Weissenberg-geometry diffractometer. Setting angles ω and Y were read for each reflection from a punched paper tape produced as output from the FORTRAN programme PAULUS 67 supplied by the manufacturer. All reflections in a hemisphere of the reciprocal lattice with $\sin\theta/\lambda \leqslant 0.64$ were measured using graphite-monochromated Mo$K\alpha$ radiation and the ω-scan technique. The crystal scan range was 2° for layers 0 to 3, inclusive, and 3° for the remaining higher layers. Background counts were made at both ends of each ω scan range, the individual counts each being for half of the scan count time.

The measured data recorded on punched paper tape were reduced to structure amplitudes using a FORTRAN programme written locally. The tape was checked for punching errors, pairs of background counts were evaluated and compared to ensure that each reflection had been completely scanned, and then were subtracted from the appropriate scan counts, and the estimated standard deviations of the observations were calculated. It was not necessary to correct for apparent crystal decomposition or movement (as indicated by the intensities of repeated measurements of standard reflections). Finally, Lorentz and polarization, but not absorption, corrections were applied. Reflections having net intensities less than twice their corresponding estimated standard deviation were designated as "unobserved" and were omitted from the data set, thereby leaving 1112 independent, non-zero observations to be used in the structure determination.

All the crystal structure analysis computations described below were performed on an IBM 7094 computer using the X-RAY 63 crystallographic programme system of Stewart *et al.*[8] and the drawing programme ORTEP written by Johnson.[9] The X-ray atomic scattering factors used in the calculation of structure factors were those listed in the *International Tables for X-Ray Crystallography*, Volume III.[10]

CRYSTAL DATA

The α-derivative. $C_{11}H_7N_2O_2Br$; $M = 279.1$. Monoclinic (b unique), $a = 19.51 \pm 0.05$ Å, $b = 9.13 \pm 0.05$ Å, $c = 13.96 \pm 0.05$ Å, $\beta = 118.0 \pm 0.5°$, $V = 2195 \pm 30$ Å³, $D_m = 1.69 \pm 0.03$ g cm⁻³, $Z = 8$, $D_c = 1.72 \pm 0.03$ g cm⁻³. Linear absorption coefficient for X-rays $[\lambda(\text{Cu}K\alpha) = 1.5418$ Å$]$, $\mu = 55.00$ cm⁻¹.[11] Number of electrons per unit cell, $F(000) = 1104$. Systematically absent reflections: hkl when $h + k$ odd, $h0l$ when h and l odd, $0k0$ when k odd; space group Cc or $C2/c$.

The β-derivative. $C_{11}H_7N_2O_2Br$; $M = 279.1$. Monoclinic (b unique), $a = 5.45 \pm 0.01$ Å, $b = 14.78 \pm 0.01$ Å, $c = 12.73 \pm 0.01$ Å, $\beta = 90.7 \pm 0.1°$, $V = 1025 \pm 3$ Å³. $D_m = 1.80 \pm 0.02$ g cm⁻³,¹ $Z = 4$, $D_c = 1.80 \pm 0.02$ g cm⁻³. Linear absorption coefficient for X-rays $[\lambda(\text{Mo}K\alpha) = 0.71069$ Å$]$, $\mu = 42.05$ cm⁻¹.[11] Number of electrons per unit cell, $F(000) = 552$. Systematically absent reflections: $h0l$ when $h + l$ odd, $0k0$ when k odd; space group $P2_1/n$.

DETERMINATION OF STRUCTURES

The coordinates of the bromine atom in each of the crystal structures were deduced from the respective three-dimensional Patterson maps. Structure factor contributions from each bromine atom were calculated using these coordinates, and appropriate isotropic temperature factors and corresponding heavy-atom electron density maps were plotted. The positions of atoms corresponding to parts of each structure could be located on the maps. Successive cycles of structure factor calculations from partial structure postulates followed by Fourier syntheses led eventually to the two complete structure solutions.

For the α-compound all the computations were made assuming the space group to be $C2/c$ (with one molecule per asymmetric unit). The successful solution and subsequent refinement (see below) confirm that this choice is correct.

REFINEMENT

$α$-*Derivative*. Full matrix least squares refinement minimizing $\sum \omega(|F_o| - G|F_c|)^2$, where ω is the weight accorded each observation, G is a variable overall scalefactor, $|F_o|$ and $|F_c|$ are corresponding observed and calculated structure amplitudes, respectively, and where the summation is over all the non-zero observations, gave an R factor [12] of 0.175. In this operation the scalefactor and atomic coordinates were varied but the isotropic temperature factor for bromine of 5.0 Å^2 and those for the other atoms of 8.0 Å^2 were held constant. A Wilson plot had indicated that the overall temperature factor was approximately 8 Å^2. Equal weights were given to all observations.

Some further cycles of refinement, in which individual atomic isotropic temperature factors were also varied with the scalefactor and coordinates,

Table 1. α-Compound. Atomic coordinates. The general equivalent positions are $\pm(x, y, z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}+y, z)$; $\pm(x, -y, \frac{1}{2}+z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$. The estimated standard deviations ($\times 10^3$) of the coordinates are given in parentheses.

Atom	x/a	y/b	z/c
Br	0.196(1)	−0.152(2)	0.074(1)
O1	0.293(4)	0.177(12)	0.182(6)
O2	0.529(5)	−0.278(11)	0.396(6)
N1	0.423(6)	−0.142(15)	0.308(7)
N2	0.410(6)	0.009(14)	0.296(8)
C1	0.317(7)	0.016(20)	0.198(10)
C2	0.294(7)	−0.132(19)	0.191(9)
C3	0.354(8)	−0.258(18)	0.221(11)
C4	0.345(7)	−0.426(18)	0.216(10)
C5	0.506(7)	−0.126(22)	0.384(10)
C6	0.534(10)	0.031(18)	0.412(12)
C7	0.618(9)	0.080(18)	0.480(11)
C8	0.618(8)	0.217(19)	0.490(10)
C9	0.551(8)	0.346(17)	0.435(9)
C10	0.481(8)	0.268(17)	0.361(11)
C11	0.475(8)	0.128(21)	0.363(10)

were computed. Unit weights were again used. Although the resulting R factor was lower, the reduction was not significant in relation to the additional parameters introduced.[13] Hence no further attempts to refine the structure were made, and the coordinates given in Table 1 and the interatomic distances and angles in Table 3 are those corresponding to the end of the first stage of refinement (thermal parameters not varied).

β-*Derivative*. The scalefactor, atomic coordinates, and individual isotropic temperature factors were varied in the initial stage of the full matrix least squares refinement, which used the same procedure as that mentioned for the α-compound. Observations were weighted according to the function $\omega = 1/\sigma(|F_o|^2)$, where $\sigma(|F_o|^2)$ is the estimated standard deviation of the square of an observed structure amplitude calculated from counting statistics only. The R factor dropped to 0.127. Refinement continued with variable anisotropic thermal parameters replacing the corresponding isotropic values and with a weighting scheme $\omega = 1/[0.02 \ F_o + \sigma(|F_o|)]^2$. The resulting R factor was 0.075. The approximate positions of all the hydrogen atoms of the structure were calculated so that they were 1.00 Å from the carbon atoms to which they were bonded, and they were all given isotropic temperature factors of 4 Å^2. None of the hydrogen atom parameters was refined in the final cycles of anisotropic least squares refinement which followed. The final R factor of 0.074 (weighted $R = 0.068$) was obtained with the parameters given in Table 2. Table 3 presents the corresponding interatomic distances and angles.

Table 2a. β-Compound. Atomic coordinates. The general equivalent positions are $\pm (x, y, z)$; $\pm (\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$. The estimated standard deviations ($\times 10^4$) of the coordinates are given in parentheses.

Atom	x/a	y/b	z/c
Br	1.0865(2)	0.1461(1)	$-0.0320(1)$
O1	0.6408(12)	0.0430(5)	0.1029(6)
O2	0.4578(14)	$-0.0792(6)$	0.1613(7)
N1	0.6061(15)	0.2776(7)	0.1588(8)
N2	0.5289(16)	0.1879(6)	0.1674(8)
C1	0.6744(17)	0.1352(8)	0.1071(9)
C2	0.8394(17)	0.1868(8)	0.0580(8)
C3	0.7926(19)	0.2751(9)	0.0929(9)
C4	0.9326(23)	0.3611(9)	0.0648(10)
C5	0.4662(19)	0.0015(9)	0.1657(9)
C6	0.3060(17)	0.0619(9)	0.2286(8)
C7	0.1153(18)	0.0207(9)	0.2860(10)
C8	$-0.0346(22)$	0.0793(10)	0.3452(11)
C9	0.0086(21)	0.1735(9)	0.3476(11)
C10	0.1927(21)	0.2156(9)	0.2887(9)
C11	0.3403(18)	0.1570(8)	0.2287(9)
H1	0.899	0.424	0.090
H2	0.903	0.387	0.061
H3	1.125	0.326	0.013
H4	0.088	-0.046	0.285
H5	-0.174	0.054	0.386
H6	-0.097	0.212	0.393
H7	0.218	0.283	0.289

Table 2b. Mean square vibration tensors, U_{ij}, ($\times 10^4$) in Å². The estimated standard deviations ($\times 10^4$) of the U_{ij} are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
Br	422(5)	412(3)	459(7)	5(3)	−18(4)	52(2)
O1	408(40)	186(43)	431(51)	8(17)	−27(20)	97(17)
O2	622(50)	241(53)	682(67)	−5(22)	−18(24)	101(22)
N1	347(45)	341(62)	464(65)	7(23)	−31(26)	9(22)
N2	376(44)	250(56)	358(59)	8(20)	−61(23)	17(20)
C1	337(49)	295(73)	391(69)	−30(28)	−41(32)	2(24)
C2	267(46)	351(70)	268(55)	1(23)	−30(26)	28(21)
C3	432(58)	285(70)	368(74)	−44(28)	−11(30)	34(26)
C4	889(88)	182(64)	849(111)	−43(38)	−83(40)	92(38)
C5	340(55)	314(76)	281(71)	11(28)	23(30)	4(24)
C6	302(50)	390(78)	280(70)	48(26)	−4(30)	22(22)
C7	287(51)	396(79)	500(86)	9(25)	−15(32)	77(26)
C8	516(65)	540(99)	467(86)	13(33)	7(37)	51(30)
C9	449(64)	393(87)	561(91)	43(28)	−16(33)	44(30)
C10	586(69)	350(77)	366(76)	92(31)	−55(32)	62(29)
C11	376(48)	177(69)	324(64)	−42(26)	2(28)	−41(22)

Lists of the observed structure amplitudes and calculated structure factors for both structure analyses may be obtained upon request from the author.

Table 3a. Some interatomic distances. The estimated standard deviations ($\times 10^2$ for the α-compound, $\times 10^3$ for the β-compound) of the distances are given in parentheses (in Ångströms).

α-Compound		β-Compound	
Br − C2	1.85(10)	Br − C2	1.877(11)
O1 − C1	1.53(21)	O1 − C1	1.375(14)
		O1 − C5	1.392(14)
O2 − C5	1.44(22)	O2 − C5	1.195(16)
N1 − N2	1.40(18)	N1 − N2	1.396(14)
N1 − C3	1.70(17)	N1 − C3	1.326(14)
N1 − C5	1.46(14)		
N2 − C1	1.68(14)	N2 − C1	1.357(14)
N2 − C11	1.60(19)	N2 − C11	1.376(14)
C1 − C2	1.41(25)	C1 − C2	1.340(15)
C2 − C3	1.56(22)	C2 − C3	1.403(17)
C3 − C4	1.54(23)	C3 − C4	1.527(18)
C5 − C6	1.52(26)	C5 − C6	1.489(16)
C6 − C7	1.53(21)	C6 − C7	1.415(16)
C6 − C11	1.36(23)	C6 − C11	1.419(17)
C7 − C8	1.26(24)	C7 − C8	1.414(18)
C8 − C9	1.66(21)	C8 − C9	1.412(20)
C9 − C10	1.45(18)	C9 − C10	1.406(18)
C10 − C11	1.28(25)	C10 − C11	1.412(17)

Table 3b. Some interatomic angles. The estimated standard deviations ($\times 10$ for the β-compound) of the angles are given in parentheses (in degrees).

α-Compound		β-Compound	
		C1 − O1 − C5	120.4(9)
N2 − N1 − C3	120(8)	N2 − N1 − C3	104.9(9)
N2 − N1 − C5	94(11)		
C3 − N1 − C5	145(13)		
N1 − N2 − C1	102(10)	N1 − N2 − C1	108.8(9)
N1 − N2 − C11	123(9)	N1 − N2 − C11	126.0(9)
C1 − N2 − C11	135(12)	C1 − N2 − C11	125.2(10)
O1 − C1 − N2	107(10)	O1 − C1 − N2	120.8(9)
O1 − C1 − C2	147(11)	O1 − C1 − C2	129.5(10)
N2 − C1 − C2	102(11)	N2 − C1 − C2	109.7(10)
Br − C2 − C1	109(9)	Br − C2 − C1	126.4(9)
Br − C2 − C3	120(10)	Br − C2 − C3	128.7(8)
C1 − C2 − C3	121(12)	C1 − C2 − C3	104.8(9)
N1 − C3 − C2	88(10)	N1 − C3 − C2	111.7(10)
N1 − C3 − C4	134(10)	N1 − C3 − C4	120.9(11)
C2 − C3 − C4	132(12)	C2 − C3 − C4	127.3(10)
		O1 − C5 − O2	116.0(10)
		O1 − C5 − C6	117.0(10)
O2 − C5 − N1	99(12)		
O2 − C5 − C6	145(11)	O2 − C5 − C6	126.9(11)
N1 − C5 − C6	115(14)		
C5 − C6 − C7	126(14)	C5 − C6 − C7	117.3(11)
C5 − C6 − C11	112(13)	C5 − C6 − C11	121.1(9)
C7 − C6 − C11	122(15)	C7 − C6 − C11	121.6(10)
C6 − C7 − C8	107(13)	C6 − C7 − C8	116.4(12)
C7 − C8 − C9	135(12)	C7 − C8 − C9	121.2(12)
C8 − C9 − C10	104(12)	C8 − C9 − C10	123.0(12)
C9 − C10 − C11	122(12)	C9 − C10 − C11	115.6(12)
N2 − C11 − C6	96(14)	N2 − C11 − C6	115.3(9)
N2 − C11 − C10	136(11)	N2 − C11 − C10	122.5(10)
C6 − C11 − C10	127(14)	C6 − C11 − C10	122.2(10)

DESCRIPTION OF THE STRUCTURES

Fig. 1 shows molecules of the two derivatives as viewed along the c-axes of the crystals, while Table 4 gives the out-of-plane distances of all the atoms of each molecule from least squares planes calculated through the appropriate benzene ring atoms. It is clear that the molecules of both derivatives are approximately planar. From this geometry and by comparison with the known hydrogen atom positions in the β-derivative, the locations of the hydrogen atoms and the double bond in the α-compound may be confidently postulated, even though the accuracy of the crystal structure analysis itself does not permit this. The results therefore confirm that the parent compounds have the structures suggested by Veibel *et al.*[3-6] and accepted by Mosby.[7]

In both crystal structures the molecules are arranged with their shortest dimensions parallel to the b-axes. The directions of the longer dimensions of the molecules make angles with the respective a-axes of about 45° and 40° for the α- and β-derivatives, respectively. All short intermolecular distances
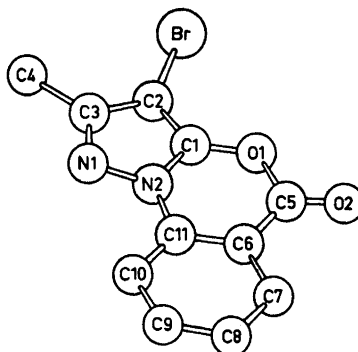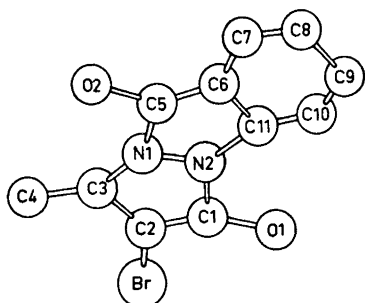
Fig. 1a. A molecule of the α-compound, as viewed along the *c* crystallographic axis.

Fig. 1b. A molecule of the β-compound, as viewed along the *c* crystallographic axis.

correspond to those expected for van der Waals packing forces. In the α-compound the shortest of 3.10 Å is in the molecular plane, between the oxygen atom, O2, and the bromine of the neighbouring molecule at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ relative to the first. From one side of each molecule there is a contact of 3.40 Å between Cl and the carbon atom, C7, of the molecule at $(1-x, y, \frac{1}{2}-z)$. On the other side there are also carbon-carbon contacts of 3.40 Å,

Table 4. Distances (in Ångströms) of atoms from the least squares planes calculated through the benzene rings. The planes are given by the equations

$$-1.22x + 3.58y + 1.38z = -9.08 \text{ (α-compound)}$$

and

$$3.369x - 1.485y + 9.831z = 3.172 \text{ (β-compound)}$$

in direct space. The estimated standard deviations of the distances are approximately 0.06 Å for the α-compound and 0.012 Å for the β-compound.

Atom	α-Compound	β-Compound
C6	− 0.03	− 0.014
C7	0.06	0.003
C8	− 0.03	0.013
C9	− 0.05	− 0.017
C10	0.09	0.005
C11	− 0.05	0.010
Br	0.40	0.042
O1	0.23	0.065
O2	0.01	− 0.074
N1	− 0.02	− 0.019
N2	0.03	0.024
C1	0.24	0.048
C2	0.01	0.051
C3	0.28	− 0.004
C4	0.16	− 0.072
C5	− 0.06	− 0.025

between C5 and C6, C5 and C11, and C6 and C6 of one molecule and its neighbour at $(1-x, -y, 1-z)$. In crystals of the β-compound there is an in-plane intermolecular contact of 3.207 Å between O2 of one molecule and C10 of the molecule at $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ relative to it. Between the molecular planes there are Br···O and C···C contacts. The shortest, of 3.155 Å, is between Br of a reference molecule and O2 of the molecule at $(1-x, -y, -z)$. There is also a Br···O1 contact of 3.297 Å between these same molecules. Finally, between C3 of a molecule and C10 of that at $(1+x, y, z)$ there is a distance of 3.407 Å.

Unfortunately, the very limited accuracy of the structure analysis of the α-derivative does not permit a meaningful comparison of the interatomic distances and angles of the two compounds. The geometry of the β-compound, however, conforms to that which might have been expected for this structure.

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