Structures of 2,4-Dinitroanisole and 2,6-Dinitroanisole

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Abstract. 2,4-Dinitroanisole, $C_7H_6N_2O_5$, $M_r = 198$, monoclinic, $P2_1/n$, $a = 8·772$ (2), $b = 12·645$ (2), $c = 15·429$ (4) Å, $\beta = 81·89$ (2)°, $V = 1694$ Å^3, $Z = 8$, D_m not determined, $D_x = 1·56$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0·7093 Å, $\mu = 1·26$ cm^{-1}, $F(000) = 816$, $T = 298$ K, $R_F = 0·075$ for 1916 observed reflections. 2,6-Dinitroanisole, $C_7H_6N_2O_5$, $M_r = 198$, triclinic, $P1$, $a = 3·854$ (1), $b = 7·736$ (2), $c = 14·476$ (4) Å, $\alpha = 89·25$ (2), $\beta = 86·97$ (2), $\gamma = 75·59$ (2)°, $V = 417$ Å^3, $Z = 2$, D_m not determined, $D_x = 1·58$ g cm^{-3}, λ(Mo $K\alpha_1$) = 0·7093 Å, $\mu = 1·28$ cm^{-1}, $F(000) = 204$, $T = 298$ K, $R_F = 0·069$ for 1046 observed reflections. In the 2,4-dinitro compound, the two independent methoxy groups make torsion angles of 5 and 13° with the ring planes, whereas in the 2,6-dinitro compound the angles are 72 and 79°. These results agree with those of related crystal structures. The rate of replacement of methoxy with an amino substituent appears to be correlated with out-of-plane twist of the methoxy group.

Introduction. The ease with which a methoxy group can be replaced by an amine in an aromatic system depends upon the nature of the substituents adjacent to the methoxy group:
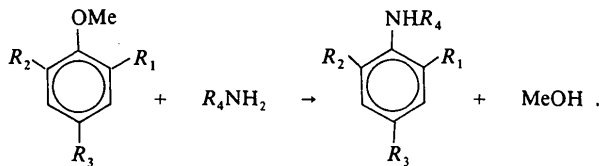
The effect of substituents on the kinetics of this reaction, however, is not simply that of steric hindrance. When the amine is cyclohexylamine or piperidine for example, and $R_1 = NO_2$, substitution is much more rapid if a bulky group such as Br, CH_3 or NO_2 is in the 6 (*i.e.* R_2) position than if it is in the 4 (R_3) position (Nudelman & Palleros, 1985). This difference in rate of reaction can be attributed to the effect which substituents R_1 and/or R_2 have on the orientation of the methoxy group with respect to the aromatic ring. To this end, we report here the crystal-structure analyses of 2,4- and 2,6-dinitroanisole, (I) and (II).

Experimental. (I) and (II) prepared as described (Nudelman & Palleros, 1981). Intensity data for (I) collected on Nonius CAD-4, for (II) on a Canberra–Picker diffractometer (with line-profile analysis; Grant & Gabe, 1978) in θ–2θ scan; no absorption correction; other details are in Table 1, Structures solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined on F by block-diagonal least-squares refinement by *NRC* PDP-8e system of programs (Larson & Gabe, 1978); anisotropic temperature factors for non-H atoms, weights $w = 1/\sigma^2(F)$, $\sigma(F)$ on counting statistics; scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms of aromatic rings given theoretical positions and those of methyl groups inferred from the position of one prominent Δp peak in each case.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 2;* bond lengths and angles are given in Table 3. The molecules are illustrated in Figs. 1 and 2.

Both unit cells contain two independent molecules, A and B, per asymmetric unit. In (I), molecule B, the *ortho* nitro group is disordered in two positions about the C—N bond (Fig. 1). The torsion angles of the nitro and methoxy groups with the aromatic ring, as determined from their least-squares planes, are given in Table 4. In the A and B molecules of 2,4-dinitroanisole the methoxy and *para* nitro groups make small angles with the benzene ring planes whereas the *ortho* nitro groups make angles of 3 and 35°.

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* Lists of structure factors, anisotropic thermal factors and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43488 (44 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Data-collection and refinement details*

	2,4-Dinitroanisole	2,6-Dinitroanisole
Crystal dimensions (mm)	0·16 × 0·24 × 0·52	0·25 × 0·3 × 0·3
No. of reflections used for lattice parameters	25	24
Their 2θ range (°)	$25 < 2\theta < 40$	$35 < 2\theta < 50$
$2\theta_{max}$ (°)	55	55
Maximum values of h, k, l	11, 16, 20	5, 10, 18
Standard reflections	$\overline{3}22, \overline{3}2\overline{1}, \overline{3}2\overline{3}$	120, 040, 006
Their variation (%)	2	3
No. of measured reflections	4136	2177
No. of unique reflections	3879	1898
R_{int}	0·02	0·02
No. of significant reflections $|I > 2 \cdot 5\sigma(I)|$	1916	1046
R_I	0·075*	0·069
wR_I	0·071	0·035
S	3·7	5·6
$(\Delta/\sigma)_{max}$	0·4	0·3
$\Delta\rho$ final ΔF map (e Å^{-3})	0·6	0·3
Secondary extinction (μm)	0·24	0·24

* The relatively high value of R for 2,4-dinitroanisole is probably due to the disordered nitro group of molecule B.
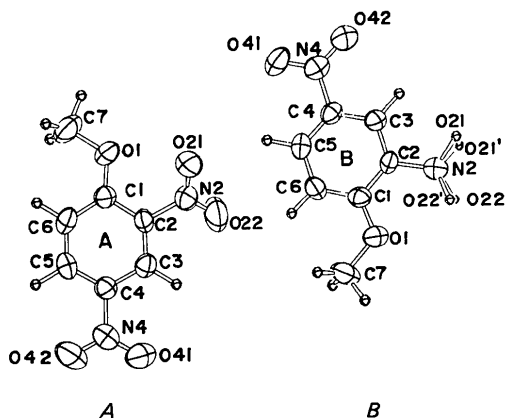

Fig. 1. *ORTEP* plot (Johnson, 1965) of molecules A and B of 2,4-dinitroanisole with 50% probability ellipsoids. (H atoms have fictitious $B = 0.8$ Å^2.) The O atoms of the disordered nitro group have fictitious $B = 1.8$ Å^2.
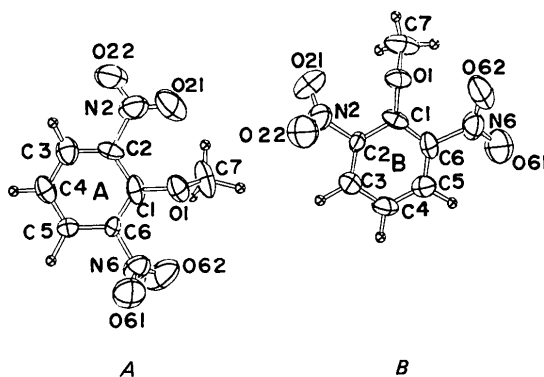

Fig. 2. *ORTEP* plot of 2,6-dinitroanisole.

In methoxyphenyl systems with no *ortho* substituents, the favoured conformation for the methoxy group is coplanar with the ring. This is borne out by a survey of 212 crystal structures (Nyburg & Faerman, 1986) and by MO calculations (Konschin, 1983). This preferred conformation brings the methoxy H atoms close to one *ortho* H atom of the ring and the former are rotated about the C—O bond to minimize this interaction. This interaction causes an increase in the

Table 2. *Atomic coordinates and B_{eq} values of non-*H*atoms*

The temperature factors for the O atoms of the disordered nitro group were fixed during the final stages of refinement.

	x	y	z	B_{eq}^*(Å^2)
2,4-Dinitroanisole				
C(A1)	0·8042 (5)	0·5758 (3)	0·0308 (3)	3·79 (23)
C(A2)	0·6935 (5)	0·5233 (3)	0·0899 (3)	3·65 (22)
C(A3)	0·6518 (5)	0·5539 (3)	0·1745 (3)	3·85 (23)
C(A4)	0·7246 (5)	0·6430 (3)	0·2017 (3)	3·94 (23)
C(A5)	0·8359 (5)	0·6958 (3)	0·1472 (3)	4·25 (25)
C(A6)	0·8729 (5)	0·6632 (4)	0·0620 (3)	4·43 (24)
C(A7)	0·9222 (7)	0·6061 (4)	−0·1157 (3)	6·7 (3)
N(A2)	0·6165 (5)	0·4279 (3)	0·06221 (22)	5·00 (22)
N(A4)	0·6860 (5)	0·6771 (3)	0·29306 (23)	5·23 (23)
O(A1)	0·8343 (4)	0·5403 (3)	−0·05116 (18)	5·31 (19)
O(A21)	0·6856 (5)	0·3706 (3)	0·00962 (22)	7·9 (3)
O(A22)	0·4864 (4)	0·4137 (3)	0·0939 (3)	8·0 (3)
O(A41)	0·5779 (4)	0·6363 (3)	0·33840 (21)	7·12 (23)
O(A42)	0·7647 (5)	0·7461 (4)	0·31846 (24)	9·1 (3)
C(B1)	0·2832 (5)	0·0763 (3)	0·1358 (3)	3·67 (22)
C(B2)	0·2325 (5)	0·0045 (3)	0·0776 (3)	3·60 (23)
C(B3)	0·2741 (5)	0·0118 (4)	−0·0114 (3)	3·77 (22)
C(B4)	0·3695 (5)	0·0921 (3)	−0·0426 (3)	3·57 (22)
C(B5)	0·4232 (5)	0·1656 (3)	0·0115 (3)	4·14 (24)
C(B6)	0·3786 (5)	0·1577 (3)	0·1007 (3)	4·21 (25)
C(B7)	0·2809 (6)	0·1427 (4)	0·2806 (3)	5·9 (3)
N(B2)	0·1298 (5)	−0·0821 (3)	0·10823 (24)	6·2 (3)
N(B4)	0·4173 (4)	0·0986 (3)	−0·13823 (22)	4·71 (21)
O(B1)	0·2376 (4)	0·0628 (3)	0·22154 (17)	4·88 (18)
O(B21)	0·0298 (8)	−0·1031 (5)	0·0586 (4)	7·64
O(B22)	0·1187 (11)	−0·1118 (6)	0·1833 (4)	7·59
O(B21')	0·1592 (12)	−0·1724 (9)	0·0658 (6)	7·41
O(B22')	0·0474 (24)	−0·0870 (12)	0·1720 (10)	6·49
O(B41)	0·3707 (5)	0·0320 (3)	−0·18430 (19)	7·222 (19)
O(B42)	0·5033 (4)	0·1701 (3)	−0·16522 (20)	6·366 (17)
2,6-Dinitroanisole				
O(1A)	0·37787	0·53419	0·07799	4·5 (3)
O(21A)	0·1031 (19)	0·8072 (9)	0·1827 (4)	8·9 (6)
O(22A)	0·2621 (20)	1·0447 (7)	0·1550 (4)	9·1 (6)
O(61A)	0·8788 (19)	0·2987 (7)	−0·0482 (5)	8·2 (5)
O(62A)	0·5375 (18)	0·3845 (8)	−0·1615 (4)	7·3 (5)
N(2A)	0·2487 (20)	0·8956 (8)	0·1343 (4)	5·8 (5)
N(6A)	0·6873 (18)	0·4127 (8)	−0·0924 (4)	5·0 (5)
C(1A)	0·4925 (20)	0·6452 (9)	0·0204 (5)	3·7 (5)
C(2A)	0·4253 (21)	0·8295 (9)	0·0428 (5)	3·5 (5)
C(3A)	0·5220 (22)	0·9480 (10)	−0·0169 (5)	4·6 (6)
C(4A)	0·6689 (22)	0·8924 (11)	−0·1023 (5)	4·4 (5)
C(5A)	0·7114 (22)	0·7207 (9)	−0·1293 (5)	3·9 (5)
C(6A)	0·6239 (19)	0·5991 (8)	−0·0661 (4)	3·0 (4)
C(7A)	0·5905 (22)	0·4562 (11)	0·1548 (5)	6·0 (7)
O(1B)	0·0388 (13)	0·2097 (6)	0·5772 (3)	4·1 (3)
O(21B)	0·3044 (19)	0·4302 (7)	0·4535 (5)	7·8 (5)
O(22B)	0·0554 (19)	0·3494 (8)	0·3391 (4)	7·9 (5)
O(61B)	0·0415 (19)	−0·0760 (8)	0·6831 (4)	8·7 (6)
O(62B)	0·4456 (21)	−0·3172 (8)	0·6558 (4)	9·5 (6)
N(2B)	0·2385 (19)	0·3170 (8)	0·4065 (4)	5·0 (5)
N(6B)	0·2824 (19)	−0·1674 (8)	0·6353 (4)	5·1 (5)
C(1B)	0·2657 (19)	0·0830 (9)	0·5238 (4)	3·4 (5)
C(2B)	0·3632 (19)	0·1274 (8)	0·4351 (4)	2·9 (4)
C(3B)	0·5624 (23)	0·0149 (9)	0·3711 (5)	4·2 (5)
C(4B)	0·6983 (23)	−0·1637 (10)	0·3988 (5)	4·7 (5)
C(5B)	0·6002 (22)	−0·2169 (10)	0·4843 (5)	4·1 (5)
C(6B)	0·3883 (22)	−0·0991 (9)	0·5437 (5)	3·8 (5)
C(7B)	0·1867 (23)	0·2743 (11)	0·6545 (5)	6·3 (7)

* B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table 3. *Bond lengths* (Å, *e.s.d.* = 0·006 Å *for* 2,4-*dinitroanisole*, 0·01 Å *for* 2,6-*dinitroanisole*) *and bond angles* (°, *e.s.d.* = 0·4° *for* 2,4-*dinitroanisole*, 0·6° *for* 2,6-*dinitroanisole*)

	Molecule A	Molecule B		Molecule A	Molecule B		Molecule A	Molecule B
2,4-Dinitroanisole								
C(1)—C(2)	1·402	1·393	C(4)—C(5)	1·369	1·376	N(2)—O(22)	1·190	1·208
C(1)—C(6)	1·377	1·387	C(4)—N(4)	1·468	1·478	N(2)—O(22')	—	1·137
C(1)—O(1)	1·333	1·338	C(5)—C(6)	1·372	1·380	N(4)—O(41)	1·211	1·210
C(2)—C(3)	1·361	1·374	N(2)—O(21)	1·188	1·271	N(4)—O(42)	1·212	1·212
C(2)—N(2)	1·475	1·454	N(2)—O(21')	—	1·323	O(1)—C(7)	1·436	1·447
C(3)—C(4)	1·388	1·360						
C(2)—C(1)—C(6)	116·8	117·5	C(3)—C(4)—N(4)	118·4	118·0	C(2)—N(2)—O(22')	—	127·7
C(2)—C(1)—O(1)	118·9	118·4	C(5)—C(4)—N(4)	119·7	119·7	O(21)—N(2)—O(22')	123·8	122·9
C(6)—C(1)—O(1)	124·3	124·1	C(4)—C(5)—C(6)	119·6	118·9	O(21')—N(2)—O(22')	—	115·9
C(1)—C(2)—C(3)	123·8	122·4	C(5)—C(6)—C(1)	121·3	120·9	C(4)—N(4)—O(41)	119·0	118·4
C(1)—C(2)—N(2)	120·2	121·4	C(2)—N(2)—O(21)	119·0	114·2	C(4)—N(4)—O(42)	117·2	117·4
C(3)—C(2)—N(2)	116·0	116·1	C(2)—N(2)—O(21')	—	114·9	O(41)—N(4)—O(42)	123·8	124·2
C(2)—C(3)—C(4)	116·7	117·9	C(2)—N(2)—O(22)	117·2	120·5	C(1)—O(1)—C(7)	118·5	117·7
C(3)—C(4)—C(5)	121·9	122·3						
2,6-Dinitroanisole								
C(1)—C(2)	1·423	1·381	C(3)—C(4)	1·362	1·412	N(2)—O(21)	1·187	1·200
C(1)—C(6)	1·345	1·401	C(4)—C(5)	1·357	1·362	N(2)—O(22)	1·210	1·220
C(1)—O(1)	1·326	1·359	C(5)—C(6)	1·392	1·346	N(6)—O(61)	1·229	1·207
C(2)—C(3)	1·357	1·349	C(6)—N(6)	1·454	1·496	N(6)—O(62)	1·202	1·215
C(2)—N(2)	1·492	1·487	O(1)—C(7)	1·451	1·431			
C(2)—C(1)—C(6)	116·1	113·4	C(3)—C(4)—C(5)	120·7	119·4	C(2)—N(2)—O(21)	121·8	118·6
C(2)—C(1)—O(1)	120·2	118·9	C(4)—C(5)—C(6)	118·9	120·7	C(2)—N(2)—O(22)	115·5	117·7
C(6)—C(1)—O(1)	122·9	127·3	C(5)—C(6)—C(1)	122·8	123·1	O(21)—N(2)—O(22)	122·7	123·5
C(1)—C(2)—C(3)	121·5	126·4	C(5)—C(6)—N(6)	119·5	117·9	C(6)—N(6)—O(61)	120·1	119·9
C(1)—C(2)—N(2)	119·8	117·6	C(1)—C(6)—N(6)	117·7	119·0	C(6)—N(6)—O(62)	115·4	116·1
C(3)—C(2)—N(2)	118·6	116·1	C(1)—O(1)—C(7)	120·1	116·9	O(61)—N(6)—O(62)	124·5	124·0
C(2)—C(3)—C(4)	119·7	116·7						

angle between the C—O bond and the C—C bond of the ring. The average from all retrieved data is 124·4°. Although 2,4-dinitroanisole would not qualify for this survey since it contains an *ortho* substituent, the appropriate angles are in complete accord: molecule A, 124·3 (4)°, molecule B, 124·1 (4)°. As is commonly the case, methoxy H atoms are rotated about the O—C bond so as to give two short and one long H⋯H intramolecular distance: molecule A, 2·40, 2·45, 3·58 Å; molecule B, 2·18, 2·59, 3·52 Å. Thus the *ortho* nitro substituent appears to have little effect on the methoxy group whereas the latter does appear to have an effect on the former, bringing it out of coplanarity with the ring. Such considerations do not apply to 2,6-dinitroanisole which has both positions *ortho* to methoxy substituted. Here, the methoxy groups in both molecules make large angles, 72 and 79°, with the ring. One of the adjacent nitro groups has a small twist from the ring plane, the other a much larger twist.

The conformations found for 2,4- and 2,6-dinitroanisole are consistent with those of other molecules containing either one or two nitro groups adjacent to methoxy. We have retrieved data for two other structures containing a single nitro group adjacent to methoxy, α-chloro-α-chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl chloride (Simon, Rogers, Saenger & Gougoutas, 1967) and methoxymethoxy-2,4-dinitrobenzene (Jones, Sheldrick, Glenn & Kirby, 1983) and one containing two nitro groups adjacent to methoxy, 2,4,6-trinitrophenetole (Gramaccioli, Destro & Simonetta, 1968).

Table 4. *Angles* (°) *between least-squares planes of benzene rings and substituents*

	Smaller of —NO₂-group torsion angles (°)	Larger of —NO₂-group torsion angles (°)	Torsion angle of methoxy group (°)	Reference
One —NO₂ group adjacent to methoxy (starred)				
2,4-Dinitroanisole, molecule A	8	33*	13	(1)
2,4-Dinitroanisole, molecule B	2	35*, −33*	5	(1)
α-Chloro-α-chlorosulfenyl-4-nitro-2,5-dimethoxyphenylacetyl chloride	–	39*	7	(2)
Methoxymethoxy-2,4-dinitrobenzene	10	51*	4	(3)
Two —NO₂ groups adjacent to methoxy				
2,6-Dinitroanisole, molecule A	13	−58	79	(1)
2,6-Dinitroanisole, molecule B	14	−58	72	(1)
2,6-Dinitrophenetole	32	61	89	(4)

References: (1) This paper; (2) Simon *et al.* (1967); (3) Jones *et al.* (1983); (4) Gramaccioli *et al.* (1968).

As seen from Table 4, when methoxy is *ortho*-substituted on one side only, the methoxy group makes only a small angle with the ring and the nitro group is twisted significantly out of the ring plane. When there are two nitro groups adjacent to methoxy, the methoxy group makes a large angle with the ring and so does one, or both, of the adjacent nitro groups.

Thus, in conclusion, it seems reasonable to assume that it is the twisting of the methoxy group out of the

plane of the aromatic ring by the presence of nitro substituents on each side, which facilitates the replacement of methoxy by an amino group.

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Structures and Absolute Configurations of (−)-6-endo-9-Dibromocamphor and (−)-7-anti-9-Dibromofenchone*

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Abstract. $C_{10}H_{14}Br_2O$, $M_r = 310.03$, Mo $K\alpha$, $\lambda\alpha_1 = 0.70930$ Å, $T = 295$ K; dibromocamphor, monoclinic, $P2_1$, $a = 7.583$ (1), $b = 11.081$ (1), $c = 6.739$ (1) Å, $\beta = 101.457$ (4)°, $V = 554.98$ (9) Å³, $Z = 2$, $D_x = 1.855$ (1) g cm⁻³, $\mu = 72$ cm⁻¹, $F(000) = 304$, $R = 0.054$ for 925 reflections; dibromofenchone, orthorhombic, $P2_12_12_1$, $a = 7.022$ (1), $b = 12.467$ (1), $c = 13.302$ (1) Å, $V = 1164.5$ (2) Å³, $Z = 4$, $D_x = 1.768$ (1) g cm⁻³, $\mu = 69$ cm⁻¹, $F(000) = 608$, $R = 0.037$ for 691 reflections. The structures and absolute configurations of the two rearrangement products of (+)-3-endo-9-dibromocamphor have been established. The molecular geometries and dimensions are similar to those of related materials: mean C—Br lengths are 1.97 (1) Å, C(1)—C(7)—C(4) bridgehead angles 95.3 (8) and 95.7 (8)°.

Introduction. Treatment of (+)-3-endo-9-dibromocamphor (1) with chlorosulfonic acid leads to a remarkable rearrangement with inversion of configuration, producing (−)-6-endo-9-dibromocamphor (2) and (−)-7-anti-9-dibromofenchone (3) (Money, 1985; Antoniadis, Hutchinson & Money, 1987). Since it was important to establish the stereochemical course of the reaction unambiguously, the present analysis was designed to determine the structures and absolute configurations of the products.

(1)

ClSO₃H

(2)   (3)

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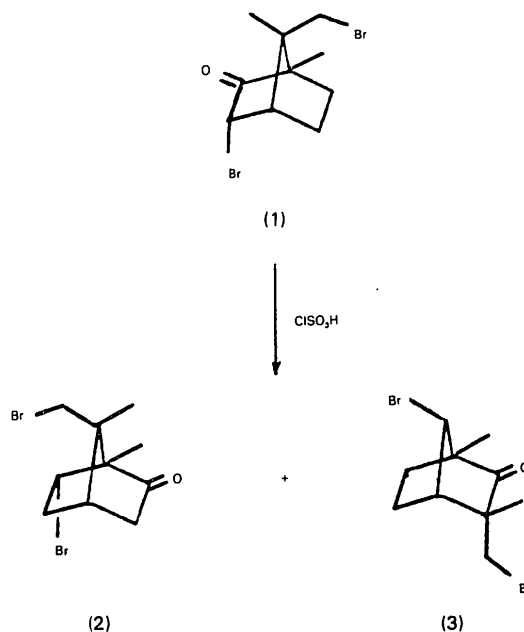
* (1S,4R,6S,7S)-6-Bromo-7-bromomethyl-1,7-dimethyl- and (1R,3R,4S,7S)-7-bromo-3-bromomethyl-1,3-dimethylbicyclo-|2.2.1|heptan-2-one.