Structure of the *trans*-Dimer of 2-Methyl-2-nitrosopropane†

Brian G. Gowenlock,* Kevin J. McCullough,* and Ross B. Manson
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS

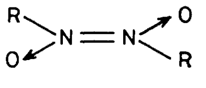
The crystal structure of the *trans*-dimer of 2-methyl-2-nitrosopropane has been established by *X*-ray diffraction studies. The crystals are monoclinic, space group $P2_1/n$, with $Z = 2$ and unit-cell constants $a = 5.929\,0(18)$, $b = 10.112(3)$, $c = 8.751(4)$ Å, and $\beta = 90.80(3)°$. Although the NN- and ON-bond distances are normal for nitroso compounds, the CN-distance was significantly longer than expected.

Only six *trans*-dimeric nitroso compounds (**1**) have been subjected to three-dimensional *X*-ray diffraction measurements.[1–5] Some older two-dimensional studies are available for R = Me[6,7] or $MeCH(Me)CH_2$.[8] In addition a number of studies have been made for *cis*-dimers (**2**)[3,9–11] and for the corresponding cyclic '*cis*-fixed' internal dimers[12–14] where the molecule can be formed only in a structure incorporating the *cis*-azodioxide functional group owing to steric constraints [*e.g.* (**3**)[12]].

It has long been recognised[15] that there are marked differences in the relative stabilities of the various *trans*-dimeric/monomeric nitrosoalkane pairs: in particular the ease of dissociation to monomer is much greater for R = tertiary alkyl than for R = secondary or primary alkyl in (**1**). It was therefore of interest to investigate whether this was reflected in structural parameters, particularly the NN-bond length. Following completion of the present study of the dimer (**1g**), structure of the related molecule (**1f**) was published.[5]

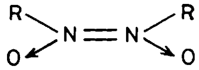
Table 1. Fractional co-ordinates of atoms with standard deviations

	x	*y*	*z*
O(1)	0.151 2(3)	0.878 16(13)	0.417 04(18)
N(1)	0.025 5(3)	0.937 63(14)	0.510 29(16)
N(1′)	−0.025 5(3)	1.062 37(14)	0.489 71(16)
C(1)	−0.069 5(3)	0.862 43(17)	0.647 27(22)
C(2)	−0.325 6(4)	0.861 21(3)	0.633 2(3)
C(3)	0.021 7(6)	0.723 51(24)	0.636 5(4)
C(4)	0.015 2(6)	0.926 7(3)	0.793 1(3)
H(1)	−0.374(6)	0.809(3)	0.711(4)
H(2)	−0.367(6)	0.821(3)	0.535(5)
H(3)	−0.392(6)	0.947(4)	0.652(4)
H(4)	−0.036(5)	0.678(3)	0.723(4)
H(5)	0.188(6)	0.718(3)	0.632(4)
H(6)	−0.025(6)	0.682(3)	0.551(4)
H(7)	−0.026(6)	0.874(3)	0.874(4)
H(8)	−0.047(5)	1.014(4)	0.806(4)
H(9)	0.173(7)	0.933(3)	0.791(4)

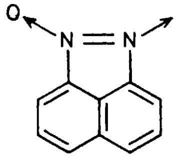


(**1**)

R
a; $O_2N[CH_2]_2$[1]
b; cyclo-C_6H_{11}[2]
c; 2-$HO_2CC_6H_4$[3]
d; 2-O_2N-cyclo-C_6H_{10}[4]
e; $O_2NCH_2CH(Ph)$[4]
f; O_2NCMe_2[5]
g; Bu^t



(**2**)



(**3**)

Experimental

trans-Dimeric 2-methyl-2-nitrosopropane (**1g**) was prepared by Stowell's method[16] and recrystallised by dissolution in methanol and cooling to −78 °C. Crystals stored at room temperature in a stoppered vessel developed a pale blue colour, presumably owing to vapourisation of the dimer followed by thermal dissociation to the monomer and subsequent condensation on the surface of the colourless crystal. Such coloured crystals could be purified rapidly by cooling to *ca.* −20 °C and evacuation. Crystals kept at 0 °C did not turn blue.

Crystal Data.—$C_8H_{18}N_2O_2$, $M = 174.2$, $a = 5.929\,0(18)$, $b = 10.112(3)$, $c = 8.751(4)$ Å, $\beta = 90.80(3)°$, $U = 524.6$ Å^3, monoclinic, space group $P2_1/n$ (non-stand. setting of No. 14), $Z = 2$, $D_c = 1.103$ g cm^{-3}, $D_o = 1.12(2)$ g cm^{-3} (flotation in CCl_4–hexane), Cu-K_α radiation ($\lambda = 1.5418$ Å), $F(000) = 192$, μ(Cu-K_α) = 6.11 cm^{-1}.

Data Collection and Reduction.—The crystal, a colourless fragment of dimensions *ca.* 0.3 × 0.4 × 0.6 mm, was mounted in a Lindeman capillary tube. Following preliminary Weissenberg photography, the intensity data were collected with an Enraf-Nonius CAD-4 diffractometer using Cu-K_α radiation and ω–2θ scanning over the range $3 < \theta \leqslant 69°$ {h 0—7, k 0—12, l −10 to +10}. Of the 982 unique reflections measured, 637 had $I > 2\sigma(I)$, where σ is the standard deviation of the background count based on counting statistics, and were used in subsequent structure solution and refinement. The intensity data were corrected for Lorentz and polarisation effects but not for absorption or crystal decay (<1%).

Structure Solution and Refinement.—The structure was solved by direct methods (SHELX 86[17]) and refined by full-matrix least-squares methods using anisotropic temperature factors for the non-hydrogen atoms (SHELX 76[18]). All hydrogen atoms were readily located on difference Fourier maps and included in subsequent refinement calculations with unrestricted positional parameters and group isotropic temperature factors. At convergence, the discrepancy indices, R and R_w, were 0.041 and 0.066 where $w^{-1} = [\sigma^2(F) + 0.0065F^2]$. The final difference map exhibited no features greater than ±0.20 e Å^{-3} with a general noise level of *ca.* ±0.07 e Å^{-3}. The final values of the refined fractional atomic co-ordinates are listed in Table 1.

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† *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Results and Discussion

Consistent with the structural formula (**1g**), the crystal structure comprises well separated dimeric units of the *trans*-configuration. There are no significant intermolecular contacts within 3.0 Å. The derived bond lengths and angles are listed in Table 2.[19]

The molecular structure is depicted in the Figure,[20] together with the numbering system adopted. Since the dimers are located at special positions, *viz.* centres of inversion, in the crystal, the molecular point group symmetry is strictly C_i, through very close to C_{2h}. The atoms O(1), N(1), C(1), and C(3) and the corresponding atoms related by the molecular inversion centre are almost coplanar. Deviations from the least-squares plane ($4.7094X + 2.6741Y + 4.6895Z = 5.0189$) through these atomic positions are within ±0.004 Å.

The N(1)–N(1′) and N(1)–O(1) bond lengths lie well within the expected ranges for *trans*-nitroso dimers (see Table 3). Similarly, there is little deviation from trigonal geometry around the central nitrogen atom. For the t-butyl substituent, the C–C distances are within 2σ of the mean value 1.514 Å, the C–H distances are in the range 0.90—0.99 Å (mean 0.95 Å) and the bond angles are close to tetrahedral. The C(1)–N(1) bond [1.533(2) Å] linking these two moieties is, however, significantly longer than the corresponding C–N distances in other nitroso compounds (Table 3), which generally have values in the region of that expected for a C–N single bond (1.47 Å).[21] This observed lengthening is most readily accounted for by the steric requirements of the bulky t-butyl group.

Table 2. Bond lengths (Å) and angles (°), with estimated standard deviations

O(1)–N(1)	1.265 0(21)	C(2)–H(3)	0.97(4)
N(1)–N(1′)	1.308 8(21)	C(3)–H(4)	0.96(3)
N(1)–C(1)	1.533 3(24)	C(3)–H(5)	0.99(3)
C(1)–C(2)	1.522(3)	C(3)–H(6)	0.90(4)
C(1)–C(3)	1.509(4)	C(4)–H(7)	0.92(4)
C(1)–C(4)	1.511(4)	C(4)–H(8)	0.96(4)
C(2)–H(1)	0.91(4)	C(4)–H(9)	0.94(4)
C(2)–H(2)	0.98(4)		
O(1)–N(1)–N(1′)	120.41(15)	H(2)–C(2)–H(3)	114.8(31)
O(1)–N(1)–C(1)	119.65(14)	C(1)–C(3)–H(4)	105.3(19)
N(1′)–N(1)–C(1)	119.93(14)	C(1)–C(3)–H(5)	114.2(19)
N(1)–C(1)–C(2)	108.51(16)	C(1)–C(3)–H(6)	112.1(22)
N(1)–C(1)–C(3)	106.10(17)	H(4)–C(3)–H(5)	112.2(27)
N(1)–C(1)–C(4)	109.01(17)	H(4)–C(3)–H(6)	109.3(30)
C(2)–C(1)–C(3)	110.23(19)	H(5)–C(3)–H(6)	103.8(29)
C(2)–C(1)–C(4)	113.02(19)	C(1)–C(4)–H(7)	108.4(22)
C(3)–C(1)–C(4)	109.74(20)	C(1)–C(4)–H(8)	111.6(21)
C(1)–C(2)–H(1)	105.5(23)	C(1)–C(4)–H(9)	109.5(23)
C(1)–C(2)–H(2)	108.2(22)	H(7)–C(4)–H(8)	109.6(31)
C(1)–C(2)–H(3)	112.8(23)	H(7)–C(4)–H(9)	109.0(32)
H(1)–C(2)–H(2)	110.0(31)	H(8)–C(4)–H(9)	108.7(31)
H(1)–C(2)–H(3)	105.1(32)		

Although the oxygen atom O(1) and the methyl group at C(3) are eclipsed [torsion angle O(1)–N(1)–C(1)–C(3) 0.7(2)°], the observed molecular conformation appears to be the least sterically demanding. The most significant intramolecular non-bonded contacts are between the oxygen atoms of the nitroso group and the hydrogens of adjacent methyl groups [O(1)–H(5) 2.31(4); O(1)–H(6) 2.53(4); O(1)–H(3′) 2.35(4); O(1)–H(8′) 2.31(4) Å]; these lie marginally within the sum of the van der Waals radii.[22] Molecular models suggest that other conformations obtained by rotation about the C–N bond, particularly the alternative coplanar arrangements in which a methyl group and the distal oxygen atom O(1′) are eclipsed, would be less favoured because of increased intramolecular steric interactions. It is, however, interesting that the 2-nitro-2-nitrosopropane dimer adopts a similar conformation as a consequence of an interaction between the nitroso oxygen and the nitrogen of the nitro substituent.[5]

For comparison, some selected geometrical data for a series of *trans*-dimeric nitroso compounds are presented in Table 3. If the earlier two-dimensional data are ignored, it appears generally that the central *trans*-dimeric framework, as judged from the N–N and N–O bond lengths, is perturbed to only a minor extent by changes in the nature of the substituent R. It is also apparent that the ease of dissociation to monomer is not reflected in the N–N length in the dimer, as would be expected from consideration of theoretical studies of the dissociation reaction.[23,24]

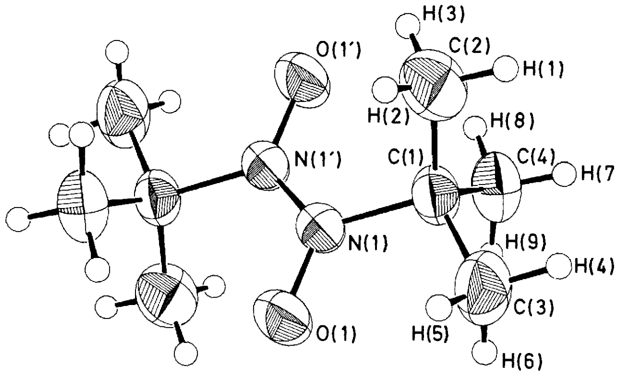

Figure. The *X*-ray molecular structure of the dimer (**1g**); non-hydrogen atoms are represented by 50% probability ellipsoids

Table 3. Bond length and angle data for *trans*-dimers (**1**)

	Lengths (Å)			Angles (°)			
R	NN	NO	CN	CNN	CNO	ONN	Ref.
$NO_2[CH_2]_2$	1.304(6)	1.262(3)	1.470(4)	117.43(41)	121.38(30)	121.14(35)	1
cyclo-C_6H_{11}	1.319(6)	1.272(6)	1.488(6)	118.4(4)	121.4(4)	120.2(4)	2
2-$HO_2CC_6H_4$	1.308(3)	1.267(3)	1.460(3)	117.1(2)	120.5(2)	122.2(2)	3
2-NO_2-cyclo-C_6H_{10}	1.302(4)	1.274(3)	1.487(2)	117.4(3)	121.4(2)	121.2(2)	4
$O_2NCH_2CH(Ph)$	1.301(4)	1.269(3)	1.479(3)	118.6(3)	120.9(2)	120.5(3)	4
O_2NCMe_2	1.329(3)	1.251(2)	1.506(2)	116.7(2)	121.2(1)	121.8(2)	5
Bu^t	1.309(2)	1.265(2)	1.533(2)	119.93(14)	119.65(14)	120.41(15)	*a*
Me	1.22	1.25	1.57	109	125	126	6[b]
Me	1.31	1.26	1.55	107.9	132.1	120	7[b]
Bu^i	1.27	1.30	1.51	117.1	120.5	122.4	8[b]

[a] This work. [b] Older two-dimensional studies; standard deviations not included.

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References

1 F. P. Boer and J. W. Turley, *J. Am. Chem. Soc.*, 1969, **91**, 1371.
2 M. Tanimura, K. Kobori, M. Kashiwagi, and Y. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1962.
3 D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *J. Am. Chem. Soc.*, 1974, **96**, 6372.
4 K. W. Chiu, P. D. Savage, G. Wilkinson, and D. J. Williams, *Polyhedron*, 1985, **4**, 1941.
5 B. Tinant, J. P. Declercq, and O. Exner, *Bull. Soc. Chim. Belges*, 1987, **96**, 149.
6 M. van Meerssche and G. Germain, *Bull. Soc. Chim. Belges*, 1959, **68**, 244.
7 H. Dietrich, personal communication, 1966.
8 H. Dietrich and D. C. Hodgkin, *J. Chem. Soc.*, 1961, 3686.
9 C. K. Prout, A. Coda, R. A. Forder, and B. Kamenar, *Cryst. Struct. Commun.*, 1974, **3**, 39.
10 G. Germain, P. Piret, and M. van Meerssche, *Acta Crystallogr.*, 1963, **16**, 109.
11 M. Azoulay and L. Trysberg, *J. Appl. Crystallogr.*, 1982, **15**, 245.
12 C. K. Prout, T. S. Cameron, R. M. A. Dunn, O. J. R. Hodder, and D. Viterbo, *Acta Crystallogr., Ser. B*, 1971, **27**, 1310.
13 F. M. Miao, D. Chantry, T. Harper, and D. C. Hodgkin, *Acta Crystallogr., Ser. B*, 1982, **38**, 3152.
14 C. K. Prout, V. P. Stothard, and D. J. Watkin, *Acta Crystallogr., Ser. B*, 1978, **34**, 2602.
15 B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.
16 J. C. Stowell, *J. Org. Chem.*, 1971, **36**, 3055.
17 G. M. Sheldrick, SHELX 86, University of Göttingen, Germany, 1986.
18 G. M. Sheldrick, SHELX 76, Cambridge, 1976.
19 R. O. Gould and P. Taylor, CALC, Edinburgh, 1983.
20 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.
21 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' Suppl. 1956–1959, ed. L. E. Sutton, Chem. Soc. Special Publication, No. 18, 1965.
22 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, New York, 1940, p. 189; L. Pauling and P. Pauling, 'Chemistry,' Freeman, San Francisco, 1975, p. 184.
23 R. Hoffman, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, 1970, **72**, 1460.
24 T. Minato, S. Yamabe, and H. Oda, *Can. J. Chem.*, 1982, **60**, 2740.

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