Crystal Structure of (*E*)-1,2-Bis(1,1-dimethyl-2-oxopropyl)diaz-1-ene-1,2-diium-1,2-diolate, the *trans*-Dimer of 3-Methyl-3-nitrosobutan-2-one

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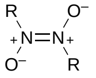
Brian G. Gowenlock and Kevin J. McCullough*

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

The solid state structure of (*E*)-1,2-bis(1,1-dimethyl-2-oxopropyl)diaz-1-ene-1,2-diium-1,2-diolate, (**3a**), the *trans*-dimer of 3-methyl-3-nitrosobutan-2-one, has been determined by X-ray crystallographic analysis; subsequent comparison of the observed geometrical parameters for **3a** with the literature values for eleven other *trans* or (*E*)-dimers suggests that there is no correlation between the N—N distances in these dimers and their respective rates of dissociation to monomer in solution.

The results of our previous X-ray crystallographic studies[1–3] of *trans*-azodioxy compounds (**1**) [*trans*- or (*E*)-dimeric nitroso compounds] along with other published structural data for related compounds indicate that the molecular geometry of the central coplanar $C_2N_2O_2$ unit varies only slightly with alteration of the organic group R despite the marked differences exhibited by these compounds in their respective dissociation equilibria in solution at room temperature. We now report the single crystal X-ray analysis of (*E*)-1,2-bis(1,1-dimethyl-2-oxopropyl)diaz-1-ene-1,2-diium-1,2-diolate (**3a**), the *trans*-dimer of 3-methyl-3-nitrosobutan-2-one, prepared by the nitrosation of 3-methylbutan-2-one[9] and recrystallised from chloroform–light petroleum (bp 60–80 °C).[6]



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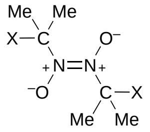

3a X = COMe
c X = CO_2Me

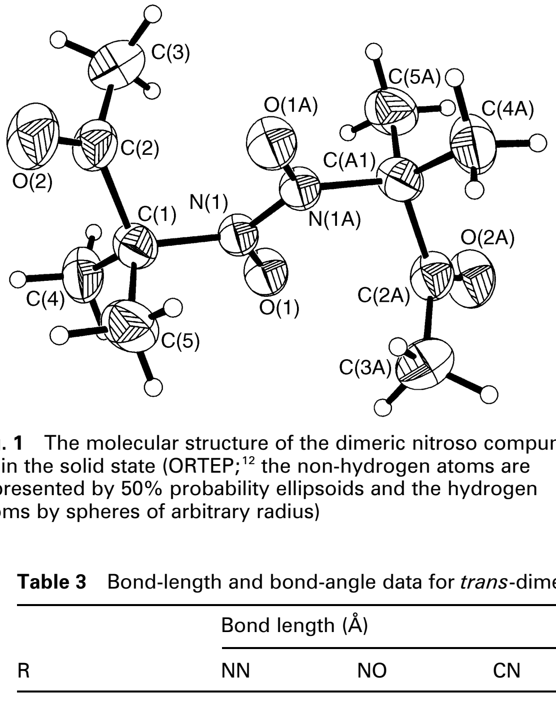

Fig. 1 The molecular structure of the dimeric nitroso compunds **3a** in the solid state (ORTEP;[12] the non-hydrogen atoms are represented by 50% probability ellipsoids and the hydrogen atoms by spheres of arbitrary radius)

The molecular structure is illustrated in Fig. 1, and the observed bond distances and angles for **3a** around the $C_2N_2O_2$ moiety are compiled along with those obtained previously for other *trans* dimers in Table 3. Molecule **3a** clearly has the *trans*- or (*E*)-configuration and, in a similar fashion to the related compound **3c**, it adopts a low symmetry C_i conformation, presumably to minimise intramolecular steric interactions between the acetyl group and the distal NO group.[3]

Analysis of the structural data in Table 3 does not reveal any strong correlations between the N—N bond length, or indeed any other geometrical parameter, in dimeric nitroso compounds and the ease of dissociation to the monomer in solution. This is particularly true for compounds **3a** and **3c** which are structurally similar but markedly different in terms of their respective rates of dissociation.[6] We conclude, therefore, that the dissociation process, although necessarily accompanied by stretching of the N—N bond, also involves other marked structural changes in the transition state as has been stated elsewhere.[21,22]

Crystal Data.—$C_{10}H_{18}N_2O_4$, $M_r = 230.3$, colourless prisms, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), $a = 6.7448(3)$, $b = 9.1438(7)$, $c = 10.3286(6)$ Å, $\beta = 104.829(12)°$, $V = 615.78(7)$ Å^3, $Z = 2$ (the dimeric molecule sits on a crystallographic centre of symmetry), $D_c = 1.242$ g cm^{-3}, $F(000) = 248$, μ(Mo-Kα) = 0.096 cm^{-1}.

The intensity data were collected on an Enraf–Nonius FAST area detector diffractometer [temperature 293(2) K; θ range 3.95–29.87°; $-9 \le h \le 6$, $-11 \le k \le 12$, $-14 \le l \le 12$]

Table 3 Bond-length and bond-angle data for *trans*-dimeric nitroso compounds $(RNO)_2$

	Bond length (Å)			Bond angles (°)			
R	NN	NO	CN	CNN	CNO	NNO	Ref.
2,6-Pr^i_2-C_6H_3	1.323(2)	1.267(2)	1.467(2)	118.16(12)	120.86(13)	120.93(13)	2
$NO_2CH_2CH_2$	1.304(6)	1.262(3)	1.470(4)	117.4(4)	121.3(3)	121.1(3)	13
cyclo-C_6H_{11}	1.319(6)	1.272(6)	1.488(6)	118.4(4)	121.4(4)	120.2(4)	14
2-HO_2C—C_6H_4	1.308(3)	1.267(3)	1.460(3)	117.1(2)	120.5(2)	122.3(2)	15
2-NO_2—C_6H_{10}	1.302(4)	1.274(3)	1.487(2)	117.4(3)	121.4(2)	121.2(2)	16
$PhCHNO_2CH_2$	1.301(4)	1.269(3)	1.479(3)	118.6(3)	120.9(2)	120.5(3)	16
Norbornan-1-yl	1.308(5)	1.269(5)	1.483(5)	119.2(3)	120.7(3)	120.1(3)	17
4-I-C_6H_4	1.316(7)	1.279(5)	1.467(6)	118.0(5)	120.3(4)	121.6(5)	18
Bu^t	1.309(2)	1.265(2)	1.533(2)	119.91(14)	119.65(14)	120.41(15)	1
Me_2C—NO_2	1.329(3)	1.251(2)	1.506(2)	116.7(2)	121.2(1)	121.9(2)	19
Me_2C—CO_2Me	1.322(3)	1.269(3)	1.504(3)	117.4(2)	122.4(2)	120.2(2)	3
Me_2C—COMe	1.318(2)	1.267(2)	1.510(2)	117.1(2)	122.19(11)	120.3(2)	This work

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*To receive any correspondence (*e-mail:* k.j.mccullough@hw.ac.uk).

using graphite-monochromated Mo-Kα X-radiation (λ 0.71073 Å) and ω-scanning.[10] The structure was solved by direct methods (SHELXS-86[11]) and refined by full-matrix least-squares methods on F^2 (SHELXTL/PC[12]) using all F_0^2 data and anisotropic temperature factors for all the non-hydrogen atoms. At convergence, the discrepancy factors R and wR^2 were 0.048 and 0.082 respectively for 851 observed intensities $[F_0 > 4\sigma(F_0)]$. The weighting scheme, $w = 1/[\sigma^2(F_0^2)]$ was found to give satisfactory analysis of variance.

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Technique used: X-ray crystallography

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Table 1: Atomic coordinates for **3a**

Table 2: Derived bond lengths and angles and torsion angles for **3a**

Table 4: Anisotropic displacement parameters for **3a**

Table 5: Hydrogen coordinates and isotropic displacement parameters for **3a**

Fig. 2: A least-squares fit of the structures of the dimeric nitroso compounds **3a** and **3c**

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