Structure of the *trans*-Dimer of 2,6-Di-isopropylnitrosobenzene

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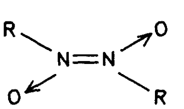
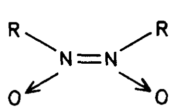
The crystal structure of the *trans*-dimer of 2,6-di-isopropylnitrosobenzene has been established by *X*-ray diffraction studies. The crystals are monoclinic, space group $P2_1/n$, with $Z = 2$ and unit-cell constants $a = 8.585\,4(10)$, $b = 10.949\,7(11)$, $c = 12.113\,5(14)$ Å, and $\beta = 94.27(1)°$. The N–O and C–N bond distances are normal for aromatic dimeric nitroso compounds but the N–N distance is significantly longer than in most *trans*-dimers due to unavoidable intramolecular steric interactions between isopropyl groups in opposite halves of the dimer.

It is well known[1] that C-nitroso compounds can exist in the three different molecular forms, the monomer R–N=O, the *trans*-dimer (A) and the *cis*-dimer (B). The relative stabilities of the forms are a function of the state, the character of the solvent in which they are placed, and the molecular environment within which the nitroso functions are located. Examples of these functions are demonstrated by (*a*) nitrosobenzene which in the solid state is the *cis*-dimer[1,2] but which in solution or gas phase is 100% monomer,[3] (*b*) 2,6-dimethylnitrosobenzene which in the solid state is the *trans*-dimer but which exists in solution in an equilibrium system,[4] and (*c*) 2,4,6-tri-t-butylnitrosobenzene which only exists as the monomer, whether in the solid state or in solution, in which the NO group is twisted out of coplanarity with the ring due to the steric constraints of the immediately adjacent t-butyl groups.[5] There is very little information available[6] concerning the chemistry of *trans*-dimeric 2,6-di-isopropylnitrosobenzene (DDIPNB) although it is possible to predict its properties from consideration of other 2,6-disubstituted nitrosobenzenes.



A



B

The effect of 2,6-disubstitution is such that in the series of disubstituents Me, Et, Pr^i, and Bu^t only the last named exhibits sufficient steric hindrance to prevent the formation of a *trans*-dimeric compound. This suggests that each *ortho*-isopropyl substituent adopts a conformation in which the methine hydrogen is located closer to the nitroso group than any of the hydrogens of the two adjacent methyl groups. In addition, it is found to be a characteristic structural feature of dimeric substituted nitrosobenzenes that the benzene rings are twisted out of coplanarity with the central, planar $C_2N_2O_2$ moiety. Such twists have been reported for *trans*-dimeric 4-bromonitrosobenzene ('slight'),[7] 2,4,6-tribromonitrosobenzene (72°)[8] and 2-nitrosobenzoic acid (73.3°).[2] It is of obvious interest to see whether these expected steric constraints are reflected in the molecular geometry of the co-planar six-atom unit $C_2N_2O_2$ for which we have shown that there is an almost constant geometry.[9]

Experimental

DDIPNB was made by the literature method,[6] the m.p., and i.r. and electronic absorption spectra being in accord with the published values.

Crystal Data for DDIPNB.—$C_{24}H_{34}N_2O_2$, $M = 382.54$, $a = 8.585\,4(10)$, $b = 10.949\,7(11)$, $c = 12.113\,5(14)$ Å, $\beta = 94.27(1)°$, $U = 1\,135.6$ Å^3, monoclinic, space group $P2_1/n$ (alt. setting of No. 14), $Z = 2$, $D_c = 1.119$ g cm^{-3}, Cu-K_α radiation ($\lambda = 1.541\,8$ Å), $F(000) = 416$, μ(Cu-K_α) = 5.21 cm^{-1}.

(a) *Data collection and reduction.* The data crystal, a colourless fragment *ca.* 0.50 × 0.45 × 0.43 mm, was mounted in a Lindeman capillary tube. The intensity data were measured on an Enraf–Nonius CAD4 diffractomer using Cu-K_α radiation and ω–2θ scanning. Of the 2 151 data collected within the quadrant $3 < \theta < 70°$, {h: −10 to +10, k: 0 to +13, l: 0 to +14}, 1 606 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 data were corrected for Lorentz and polarisation effects, but not for absorption or crystal decay (both <1%).

(*b*) *Structure solution and refinement.* The positions of the non-hydrogen atoms were determined by direct methods (SHELXS 86).[10] The hydrogen atoms were subsequently located on a series of difference Fourier maps. Refinement of the structure was carried out by full-matrix least-squares techniques (SHELX 76)[11] with anisotropic temperature factors for the non-hydrogen atoms. The hydrogens were included in the refinement calculations with unrestricted positional parameters and group isotropic temperature factors. At convergence, the discrepancy factors R and R_w were 0.057 and 0.079 respectively, where $w^{-1} = [\sigma^2(F) + 0.011\,07(F)^2]$. The final difference Fourier map showed no features greater than ±0.21 e Å^{-3}: the general noise level was *ca.* ±0.15 e$^-$ Å^{-3}. The final values of the refined fractional co-ordinates are compiled in Table 1. Incidental crystallographic calculations were carried out using the program CALC.[12]

Results and Discussion

The molecular structure of DDIPNB as determined by *X*-ray crystallographic analysis† is depicted in Figure 1 together with the numbering system adopted in this study. The derived bond distances and angles are listed in Table 2.

As anticipated, the crystal structure consists of well-separated dimers which have the *trans*-configuration. Apart from a soft contact [2.43(3) Å] between the nitroso group oxygen atom and an isopropyl group hydrogen related to H(12B) by the symmetry operation $-x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$, there were no significant intermolecular contacts within 3.4 Å. Although very close to

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† For details of deposition of crystallographic data see Instructions for Authors (1989), *J. Chem. Soc., Perkin Trans. 2*, 1989, Issue 1.

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

	x	y	z
N(1)	0.977 24(14)	0.027 69(12)	0.953 02(11)
O(1)	1.075 71(14)	0.061 66(14)	0.886 44(11)
C(1)	0.809 18(17)	0.044 33(15)	0.925 94(14)
C(2)	0.731 81(20)	−0.045 77(16)	0.862 15(14)
C(3)	0.571 38(21)	−0.028 39(19)	0.836 63(17)
C(4)	0.495 67(21)	0.073 39(21)	0.872 43(18)
C(5)	0.578 66(22)	0.163 11(19)	0.931 14(17)
C(6)	0.739 02(19)	0.152 11(16)	0.958 68(14)
C(7)	0.826 48(22)	0.254 15(17)	1.020 66(16)
C(8)	0.782 8(3)	0.261 2(3)	1.139 80(21)
C(9)	0.803 7(4)	0.376 36(23)	0.961 1(3)
C(10)	0.812 48(21)	−0.155 73(17)	0.818 09(16)
C(11)	0.751 5(3)	−0.275 52(21)	0.862 34(22)
C(12)	0.801 0(4)	−0.155 91(25)	0.691 72(21)
H(4)	0.382(3)	0.078 2(23)	0.859 2(22)
H(8A)	0.675(3)	0.292(3)	1.142 0(24)
H(8B)	0.847(3)	0.323(3)	1.181(3)
H(8C)	0.792(3)	0.173(3)	1.182(3)
H(9A)	0.689(4)	0.404(3)	0.967(3)
H(9B)	0.823(4)	0.367(3)	0.880(3)
H(9C)	0.870(4)	0.439(3)	1.001(3)
H(11A)	0.632(4)	−0.285(3)	0.839(3)
H(11B)	0.768(4)	−0.275(3)	0.947(3)
H(11C)	0.816(3)	−0.347(3)	0.839 1(24)
H(12A)	0.694(4)	−0.156(3)	0.664(3)
H(12B)	0.864(3)	−0.231(3)	0.667(3)
H(12C)	0.843(4)	−0.083(3)	0.669 3(25)
H(3)	0.510 2(25)	−0.094 6(22)	0.793 1(19)
H(5)	0.521(3)	0.233 6(22)	0.954 6(23)
H(7)	0.937(3)	0.237 1(19)	1.020 8(19)
H(10)	0.921(3)	−0.144 2(18)	0.835 0(18)

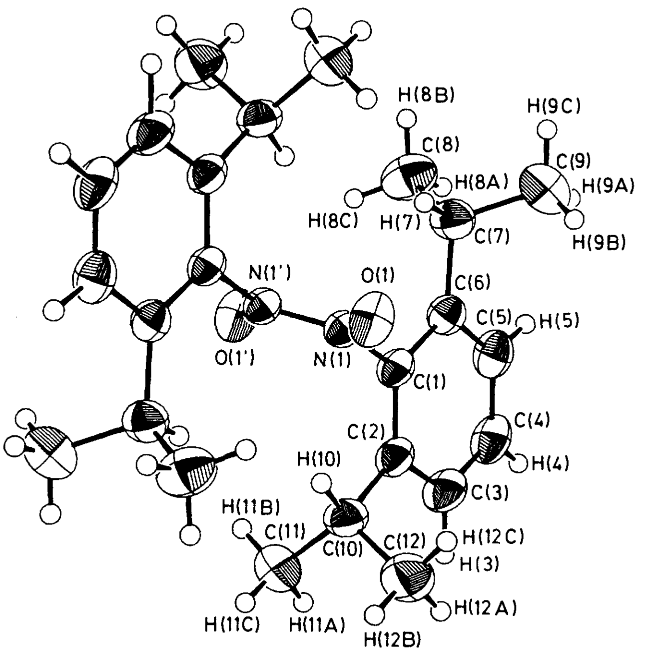

Figure 1. Molecular structure of 2,6-di-isopropylnitrosobenzene dimer (ORTEP,[18] 50% ellipsoids).

Table 2. Derived geometrical parameters for 2,6-di-isopropylnitrosobenzene.

(*a*) Bond lengths (Å) with standard deviations

N(1)–O(1)	1.266 9(19)	C(7)–H(7)	0.967(23)
N(1)–N(1′)	1.322 8(18)	C(8)–H(8A)	0.99(3)
N(1)–C(1)	1.467 0(21)	C(8)–H(8B)	0.99(3)
C(1)–C(2)	1.391 1(24)	C(8)–H(8C)	1.10(3)
C(1)–C(6)	1.395 9(23)	C(9)–H(9A)	1.04(3)
C(2)–C(3)	1.402(3)	C(9)–H(9B)	1.01(3)
C(2)–C(10)	1.506 4(25)	C(9)–H(9C)	0.99(4)
C(3)–C(4)	1.376(3)	C(10)–C(11)	1.524(3)
C(3)–H(3)	1.019(23)	C(10)–C(12)	1.527(3)
C(4)–H(4)	0.97(3)	C(10)–H(10)	0.949(22)
C(4)–C(5)	1.380(3)	C(11)–H(11A)	1.05(3)
C(5)–C(6)	1.397(3)	C(11)–H(11B)	1.02(3)
C(5)–H(5)	0.97(3)	C(11)–H(11C)	1.01(3)
C(6)–C(7)	1.513 9(25)	C(12)–H(12A)	0.95(4)
C(7)–C(8)	1.520(3)	C(12)–H(12B)	1.04(3)
C(7)–C(9)	1.526(4)	C(12)–H(12C)	0.92(3)

(*b*) Bond angles (°) with standard deviations

O(1)–N(1)–N(1′)	120.93(13)	C(7)–C(8)–H(8B)	110.0(18)
O(1)–N(1)–C(1)	120.86(13)	C(7)–C(8)–H(8C)	112.8(16)
N(1′)–N(1)–C(1)	118.16(12)	H(8A)–C(8)–H(8B)	103.9(25)
N(1)–N(1′)–O(1′)	120.93(13)	H(8A)–C(8)–H(8C)	109.1(24)
N(1)–C(1)–C(2)	117.20(14)	H(8B)–C(8)–H(8C)	110.7(24)
N(1)–C(1)–C(6)	118.65(14)	C(7)–C(9)–H(9A)	108.6(18)
C(2)–C(1)–C(6)	123.99(15)	C(7)–C(9)–H(9B)	109.9(20)
C(1)–C(2)–C(3)	116.54(16)	C(7)–C(9)–H(9C)	108.9(22)
C(1)–C(2)–C(10)	123.40(15)	H(9A)–C(9)–H(9B)	108.4(27)
C(3)–C(2)–C(10)	120.03(16)	H(9A)–C(9)–H(9C)	105.9(28)
C(2)–C(3)–C(4)	121.31(18)	H(9B)–C(9)–H(9C)	114.9(29)
C(2)–C(3)–H(3)	118.5(13)	C(2)–C(10)–C(11)	112.59(17)
C(4)–C(3)–H(3)	120.1(13)	C(2)–C(10)–C(12)	111.06(17)
C(3)–C(4)–H(4)	118.7(16)	C(2)–C(10)–H(10)	106.7(13)
C(3)–C(4)–C(5)	120.07(19)	C(11)–C(10)–C(12)	110.69(19)
H(4)–C(4)–C(5)	121.1(16)	C(11)–C(10)–H(10)	113.4(13)
C(4)–C(5)–C(6)	121.57(18)	C(12)–C(10)–H(10)	101.9(13)
C(4)–C(5)–H(5)	117.4(15)	C(10)–C(11)–H(11A)	110.0(17)
C(6)–C(5)–H(5)	121.0(15)	C(10)–C(11)–H(11B)	108.8(18)
C(1)–C(6)–C(5)	116.32(16)	C(10)–C(11)–H(11C)	111.1(17)
C(1)–C(6)–C(7)	123.80(15)	H(11A)–C(11)–H(11B)	109.4(25)
C(5)–C(6)–C(7)	119.88(16)	H(11A)–C(11)–H(11C)	113.0(24)
C(6)–C(7)–C(8)	111.10(17)	H(11B)–C(11)–H(11C)	104.3(25)
C(6)–C(7)–C(9)	111.81(18)	C(10)–C(12)–H(12A)	109.7(22)
C(6)–C(7)–H(7)	108.0(13)	C(10)–C(12)–H(12B)	106.9(16)
C(8)–C(7)–C(9)	111.85(19)	C(10)–C(12)–H(12C)	107.3(20)
C(8)–C(7)–H(7)	108.6(13)	H(12A)–C(12)–H(12B)	114.0(28)
C(9)–C(7)–H(7)	105.2(13)	H(12A)–C(12)–H(12C)	106.8(30)
C(7)–C(8)–H(8A)	109.9(18)	H(12B)–C(12)–H(12C)	111.9(26)

C_{2h}, the dimers adopt a strict C_i point group symmetry in the solid state with the molecular and crystallographic inversion centres coincident, as required by the occupancy of the unit cell.

The least-squares plane [$0.1697x + 0.7654y + 5.4414z = 5.6111$] through atoms of the $C_2N_2O_2$ moiety exhibits a high degree of planarity (mean deviation ±0.005 Å) and is essentially orthogonal to the plane of the aromatic ring (interplanar angle 88.0°). This twist from co-planarity is greater than for other *trans*-dimers of substituted nitrosobenzenes.[2,7,8]

In general, the N(1)–N(1′), N(1)–O(1), and N(1)–C(1) bond lengths for the title compound lie within the ranges generally expected for aromatic and aliphatic *trans*-nitroso dimers (see Table 3), the sp^2 C–N length being slightly shorter than the sp^3 C–N length as expected. Comparison of the crystal structures of the 2-nitrosobenzoic acid[2] and 2,6-di-isopropylnitrosobenzene dimers indicates that, although the corresponding N–O and C–N distances are similar, the central N–N distance in the latter is significantly longer. This observed lengthening of the N–N bond arises as a consequence of unavoidable intramolecular steric interactions between isopropyl groups in opposite halves of the dimer. Nonetheless, there are only minor angular deviations from a trigonal geometry around the central nitrogen atoms and the geometrical parameters for the remaining non-

Table 3. Bond length and bond angle data for *trans*-dimeric nitrosocompounds.

	Bond lengths/Å			Bond angles/°			
R	NN	NO	CN	CNN	CNO	ONO	Ref.
$NO_2CH_2CH_2$	1.304(6)	1.262(3)	1.470(4)	117.43(41)	121.38(30)	121.14(35)	13
c-C_6H_{11}	1.319(6)	1.272(6)	1.488(6)	118.4(4)	121.4(4)	120.2(4)	14
o-C_6H_4COOH	1.308(3)	1.267(3)	1.460(3)	117.1(2)	120.5(2)	122.2(2)	2
$2NO_2{\cdot}C_6H_{10}$	1.302(4)	1.274(3)	1.487(2)	117.4(3)	121.4(2)	121.2(2)	15
$Ph{\cdot}CHNO_2{\cdot}CH_2$	1.301(4)	1.269(3)	1.479(3)	118.6(3)	120.9(2)	120.5(3)	15
$Me_2C{\cdot}NO_2$	1.329(3)	1.251(2)	1.506(2)	116.7(2)	121.2(1)	121.8(2)	16
Bu^t	1.309(2)	1.265(2)	1.533(2)	119.93(14)	119.65(14)	120.41(15)	9
2,6–$Pr^i{}_2C_6H_3$	1.323(2)	1.267(2)	1.467(2)	118.16(12)	120.86(13)	120.93(13)	*a*

[a] This paper.

hydrogen atoms are normal. The refined carbon–hydrogen bond distances were in the range 0.92–1.10 Å.

The *ortho*-isopropyl groups adopt similar conformations in which the tertiary hydrogen atoms H(7) and H(10) are directed towards the nitroso group but lie out of the plane of the aromatic ring by −0.18 and −0.15 Å, respectively, in the direction of the nitroso group oxygen atom O(1) [torsion angles C(1)–C(6)C(7)–H(7) 9.9(14)° and C(1)–C(2)–C(10)–H(10) −6.7(14)°]. This conformation which is close to that which would be intuitively favoured, results in the formation of a cavity which can readily accommodate the nitroso, or indeed any structurally similar, group.

Given the high degree of steric congestion in the region of the nitroso group and the polarised nature of the N–O bond, it is not unexpected that the most significant intramolecular non-bonded contacts occur between the comparatively electrophilic nitrogen atom N(1) of the nitroso group and the hydrogen atoms H(7) and H(10) of the adjacent isopropyl groups [2.469(23) and 2.390(22) Å, respectively]. Since the corresponding distances O(1)–H(7) and O(1)–H(10) are greater than the sums of the van der Waals radii, there appears to be minimal interaction between the oxygen atom of the nitroso group and the isopropyl group hydrogen atoms. In addition, there are no appreciably short, intramolecular non-bonded contacts between the monomeric units.

There is only one other case[16] of a *trans*-dimeric nitroso compound with a N–N bond length greater than 1.320 Å and this also is related to steric packing effects. As emphasised previously[9] there is no simple correlation of N–N bond length with ease of dissociation to monomeric C-nitroso compounds. DDIPNB only dissociates to a very small extent (about 2%) in methanol solution at room temperature as judged by its absorption in the visible, $\lambda_{max.}$ 785 nm.[17]

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