Crystal Structure of Nitrosobenzene Dimer. *cis*-Azobenzene Dioxide

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Summary The crystal structure of the colourless nitrosobenzene dimer shows a *cis*-arrangement of the two nitroso-groups and an unexpected, slight non-planarity of the central $(CNO)_2$ group.

NITROSO-ALKANES dimerize readily to azo-dioxides which, both in the crystalline state and in solution,[1] are sufficiently stable for study. Thus nitrosomethane, a blue (presumably monomeric) substance at the temperature of liquid oxygen, dimerizes on warming to the colourless *cis*-azo-dioxide (Ia).[2] (Ia) is converted into the more stable *trans*-isomer (IIa) when allowed to stand in a non-polar solvent or when

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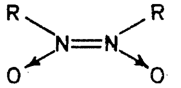
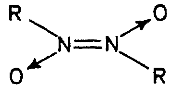
heated above its m.p. The structures of (Ia) and (IIa) have been established by crystallographic methods.[3]



(I)a; R = Me, m.p. 97°
b; R = Ph
c; R = α-$C_{10}H_7$



(II) a; R = Me, m.p. 122°
b; R = $CH_2CH_2NO_2$

The reported dimers of *p*-bromonitrosobenzene[4] and of 2,4,6-tribromonitrosobenzene[5] have *trans*-azo-dioxide structures as determined by *X*-ray analysis about twenty years ago; the *cis*-isomers are unknown. Lüttke[6] concluded that of the twenty aromatic nitroso-compounds capable of forming both *cis*- and *trans*-dimers, all had dimers with the *trans*-azo-dioxide structure except (Ib), the dimer of nitrosobenzene and (Ic), that of α-nitrosonaphthalene. These two compounds were believed to exist in the solid state as *cis*-isomers, the *trans*-isomers being unknown. As aromatic nitroso-compounds are largely dissociated to monomers in solution, structural conclusions had to be based on the spectra of solid samples in KBr discs. As the interpretation of spectra of solids may be complicated by intermolecular interactions,[7] an independent determination of the structure of the familiar dimer of nitrosobenzene by *X*-ray analysis is therefore reported here and shows the dimer to be *cis* (Ib).

Nitrosobenzene crystallizes as well-formed colourless parallelepipeds m.p. 68—69°. *Crystal data*: $C_{12}H_{10}N_2O_2$, $M = 214{\cdot}36$, orthorhombic, $a = 10{\cdot}460(3)$, $b = 13{\cdot}833(3)$, $c = 15{\cdot}156(5)$ Å, $Z = 8$; systematic absences, $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, $hk0$, $h + k = 2n + 1$, lead unambiguously to the space group *Pbcn* (No. 60). These results are in agreement with those reported previously by Hulme.[8] Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer (Cu-K_α radiation). In total, 1054 independent reflections were judged to be significantly above background. The structure was solved by the symbolic addition method,[9] and the model, including hydrogen atoms, has been refined by full-matrix least-squares methods to a final *R*-factor of 0·057 on all observed data. A stereoscopic view of the molecular structure is shown (Figure).

A detailed comparison of bond lengths in the nitroso-groups is only justified in the case of the *trans*-dimer of 2-nitronitrosoethane (IIb),[10] where the N–O, N–N, and C–N lengths were 1·262(3), 1·304(6), and 1·470(4) Å, respectively, compared to 1·264(4), 1·323(5), and 1·454(5) Å in the present structure. The bond angles around nitrogen in (Ib) are all within 1·2° of 120°. The six atoms of the central $(CNO)_2$ group in the nitrosobenzene dimer are very much less planar than the corresponding atoms in (IIb). In nitrosobenzene, the torsion angle C(phenyl)–N–N–C-(phenyl) is 17·9° and that of O–N–N–O is 4·0°. The non-planarity of this group of atoms can be described as a pyramidal displacement of the two nitrogen atoms by 0·029 and 0·030 Å on *opposite* sides of the best plane through the two oxygen and the two bonded carbon atoms; the corresponding distances in (IIb) were $\pm 0{\cdot}010$ Å. No meaningful comparisons can be made with other nitroso-dimers on account of the low accuracy of the results available. The benzene rings are accurately planar and make angles of 64·8 and 111·7° with the best plane through the four central carbon and oxygen atoms. The dihedral angle between the two benzene rings is 62·8°. The nitrogen atoms deviate by 0·037 and 0·036 Å, respectively, from the best plane through the benzene ring to which each is attached.

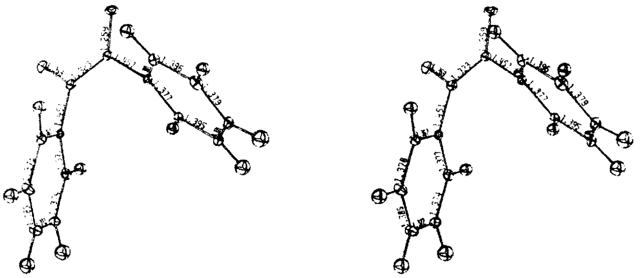


FIGURE. *Stereoscopic picture of the* cis-*dimer of nitrosobenzene. The standard deviations of the* C–C *lengths are approximately* 0·006 Å.

There remains the question of why, among the aromatic compounds investigated, the dimers of only nitrosobenzene and α-nitrosonaphthalene have been found in the *cis*-configuration. The answer probably lies in an understanding of the possibilities for crystal packing of these stereoisomers since the i.r. spectrum of pure (Ib) just above its m.p. shows, in addition to the monomer bands previously noted,[11] an absorption at 1400 cm^{-1} attributable to the *cis*-dimer and a substantially stronger peak at 1263 cm^{-1} indicative of the *trans*-dimer. These two peaks appear (but at lower relative intensities) in the spectrum of the melt at 90° previously reported[11] by Lüttke. It seems likely, then, that the melt contains, in addition to the monomer, significant amounts of both *trans*- and *cis*-dimers.

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