

Control experiments on stabilities of the isomers of **17**, carried out by subjecting **17m** and **17o** + **17p** to the reaction of **1** with silver hexafluoroantimonate in toluene and benzene-toluene, showed that small amounts of isomerization of **17o** and **17p** could occur under those conditions.⁶⁰

Reaction of **1** with silver hexafluoroantimonate in chlorobenzene-benzene with added tetramethylurea gave 71% silver chloride and 92% barium carbonate. Glpc analyses (column D, 220°) gave a 36% yield of **18**, a 21% yield of isomers of **14**, and (column A, 125°) a 20% yield of 1-chloroapocamphane.

Reaction of **4** with silver hexafluoroantimonate in chlorobenzene-benzene with added tetramethylurea gave 73% silver chloride and 89% barium carbonate. Glpc analyses (column B, 235°) indicated a 29% yield of 1-phenylapobornylene (**20**), an 18% yield of isomers of **13**, and (column B, 110°) a 33% yield of 1-chloroapobornylene.

Products **13** and **20** were collected by preparative glpc (column D, 235°), and the two peaks of longer retention time were proved to be isomers of **13** by the identity of their nmr spectrum with that of assigned material (*vide supra*). The component of shorter retention

time was purified by distillation to give **20**: ir (film) 3050 (m), 1605 (w), 1580 (w), 760 (s), 740 (m), 720 (s), and 695 (s) cm⁻¹; nmr (CCl₄) 0.73 and 0.75 (both s, 6, C(CH₃)₂), 1.17 (m, 2, CH), 1.97-2.45 (m, 3, CH), 6.01 (AMX, *J*_{AM} = 6 Hz, *J*_{AX} = 1 Hz, 1, H_A-C=C), 6.08 (AMX, *J*_{AM} = 6 Hz, *J*_{MX} = 3 Hz, 1, H_M-C=C), and 7.21 (m, 5, Ar H); mass spectrum *m/e* 198 (M⁺, 38), 183 (M⁺ - CH₃, 58), 155 (M⁺ - CH₃CHCH₃, 97), and 91 (100).

Anal. Calcd for C₁₃H₁₈: C, 90.85; H, 9.15. Found: C, 90.56; H, 9.09.

The identity of 1-chloroapobornylene was established from the similarity of its nmr spectrum to the material from the chlorobenzene reaction above, after preparative glpc (120°, column D).

Acknowledgments. Support for these studies was provided by the National Institutes of Health and the National Science Foundation. Mass spectral processing equipment was provided by grants from the National Institutes of Health. We are grateful for this support.

Structural Studies on Nitrosobenzene and 2-Nitrosobenzoic Acid. Crystal and Molecular Structures of *cis*-Azobenzene Dioxide and *trans*-2,2'-Dicarboxyazobenzene Dioxide^{1,2}

David A. Dieterich, Iain C. Paul,* and David Y. Curtin*

Contribution from the Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. Received April 11, 1974

Abstract: A spectroscopic and X-Ray structural study of crystalline nitrosobenzene and 2-nitrosobenzoic acid has been undertaken. A structure analysis of crystalline nitrosobenzene revealed that the familiar colorless crystals, which exist in two distinct habits, contained exclusively the *cis*-azobenzene dioxide (**3a**) molecule. This result was consistent with the infrared spectroscopic correlation proposed by Lüttke. An infrared examination of the melt of nitrosobenzene showed the presence of bands in the infrared indicative of the *trans*-azobenzene dioxide (**3b**) molecule. Attempts to obtain stable crystals of this dimer were unsuccessful. The crystals of **3a** are orthorhombic, *a* = 10.460 (3), *b* = 13.833 (3), *c* = 15.156 (5) Å, and there are eight molecules in the unit cell, space group *Pbcn*. The structure was refined to an *R* factor of 0.060 on 1084 nonzero reflections. The molecule has approximate C₂ symmetry; the N-N and N-O lengths are 1.321 (5) and 1.265 (4) Å (av). There is considerable out-of-plane distortion at nitrogen, resulting in C-N-N-C and O-N-N-O torsion angles of 18.0 and 3.9°. The X-ray analysis of crystalline 2-nitrosobenzoic acid showed that it exists in the crystal as *trans*-2,2'-dicarboxyazobenzene dioxide (**4**). This result was also consistent with Lüttke's correlation. The crystals are triclinic: *a* = 7.623 (4), *b* = 7.412 (4), *c* = 6.746 (4) Å; α = 115.14 (4), β = 106.66 (4), γ = 94.20 (4)°. This space group is *P* $\bar{1}$ with one molecule in the unit cell. The structure was refined to an *R* factor of 0.052 on 880 nonzero reflections. The dimer molecule has exact crystallographic C_i symmetry; the N-N and N-O lengths are 1.308 (3) and 1.267 (3) Å. In **4** there is much less out-of-plane distortion; the C-N-N-O torsion angle is 5.5°. The two C-O lengths are 1.301 (3) and 1.218 (3) Å and the C-C-O angles are 114.1 (2) and 122.5 (2)°. An analysis of corresponding published dimensions for aromatic carboxylic acids shows a wide range of values. There is a linear correlation between Δr (the difference in C-O lengths) and $\Delta\theta$ (the difference in C-C-O angles). It appears that there is essentially a continuum of these values among the published structures of aromatic carboxylic acids from completely ordered (with large values of Δr and $\Delta\theta$) to those that show statistical twofold disorder. The developed crystal faces exhibited by **3a** and **4** have been analyzed in terms of the molecular packing.

The range of structural behavior and the varied properties of aromatic C-nitroso compounds,³⁻⁶

(1) Taken from the Ph.D. thesis of David A. Dieterich, submitted to the University of Illinois, 1973, available from University Microfilms, Ann Arbor, Mich.

(2) We are indebted to the National Science Foundation (NSF-GH-33634) and to the Advanced Research Projects Agency of the Department of Defense (Contract ARPA-HC-15-67-0221) for support of this work. We also acknowledge the award of an NSF fellowship to D. A. D. (1970-1973).

(3) B. G. Gowenlock and W. Lüttke, *Quart. Rev. Chem. Soc.*, **12**, 321 (1958).

(4) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, Chapter 13.

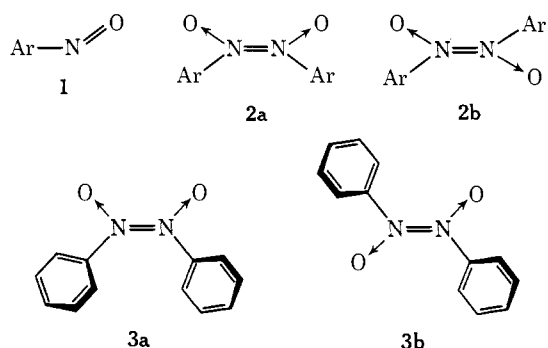
both in solution and in the crystalline state, provide a fruitful area for a combined crystallographic and chemical study.⁷ Aromatic C-nitroso compounds can exist as blue or green colored monomers (**1**) or colorless dimers (**2**). In the dimeric state, *cis* (**2a**) and *trans* (**2b**) isomers are possible. As a general rule, but one with

(5) C. N. R. Rao and K. R. Bhaskar in "The Chemistry of the Nitro and Nitroso Groups," Part 1, H. Feuer, Ed., Interscience, New York, N. Y., 1968, Chapter 3.

(6) J. H. Boyer in ref 5, Chapter 5.

(7) A preliminary communication on part of this work has been published: D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *Chem. Commun.*, 1710 (1970).

some exceptions, solutions and melts of aromatic nitroso compounds are colored blue and green, and hence contain principally monomer (there is probably a monomer \rightleftharpoons dimer equilibrium lying heavily toward monomer), whereas most crystals are colorless and contain dimers. However, several aromatic nitroso compounds have been isolated as green solids,⁸ and some have been isolated in both a green and a colorless crystalline modification.⁹ On the basis of ir studies on KBr disks of 20 aromatic nitroso compounds, Lüttke¹⁰ proposed that the presence of one band in the 1253–1299-cm⁻¹ region was characteristic of a trans dimer (2b) in the crystal, whereas two bands (one at 1389 cm⁻¹ and the other at 1409 cm⁻¹) were typical of a cis dimer (2a). The predictions of this correlation were consistent with the crystallographic data then available, as were those from a somewhat similar correlation for aliphatic nitroso compounds. Nitrosobenzene dimer was one of two aromatic nitroso compounds thus assigned the *cis*-azobenzene dioxide structure (3a) in the crystalline state.



The structural data available on aromatic nitroso compounds were few. In the main, they also date from a time when, because of reliance on the presence of heavy atoms in the molecule and on film methods for data collection, the precision obtained for the results was quite low. Crystalline 4-bromonitrosobenzene¹¹ and 2,4,6-tribromonitrosobenzene¹² have been shown to exist as *trans*-azo dioxide dimers while 4-iodonitrosobenzene was demonstrated to be monomeric.^{13,14} A microwave study of nitrosobenzene in the vapor phase is consistent with a planar, monomeric structure.²¹

(8) E. Bamberger and W. Ham, *Justus Liebig's Ann. Chem.*, **382**, 82 (1911); A. Baeyer and E. Knorr, *Chem. Ber.*, **35**, 3034 (1902).

(9) L. I. Smith and F. L. Taylor, *J. Amer. Chem. Soc.*, **57**, 2460 (1935); S. Cannizaro and A. Andreocci, *Gazz. Chim. Ital.*, **261**, 30 (1896).

(10) W. Lüttke, *Z. Elektrochem.*, **61**, 976 (1957).

(11) C. Darwin and D. C. Hodgkin, *Nature (London)*, **166**, 827 (1950).

(12) C. P. Fenimore, *J. Amer. Chem. Soc.*, **72**, 3226 (1950).

(13) M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

(14) The situation regarding X-ray work among aliphatic nitroso compounds was much better. X-ray studies on dimers of nitroso-methane,^{15,16} nitrosoisobutane,¹⁷ 2-nitronitrosoethane,¹⁸ and nitroso-cyclohexane¹⁹ have been reported. Apart from nitroso-methane, where crystals of both *trans*¹⁵ and *cis* dimers¹⁶ have been studied, all other dimers had the *trans* geometry. There is also mention²⁰ of a *cis* dimer in the structure of 1,4-dichloro-1,4-dinitrosocyclohexane having been studied by X-ray methods.

(15) M. Van Meerse and G. Germain, *Bull. Soc. Chim. Belg.*, **68**, 244 (1959).

(16) G. Germain, P. Piret, and M. Van Meerse, *Acta Crystallogr.*, **16**, 109 (1963).

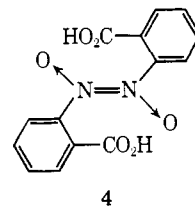
(17) H. Dietrich and D. C. Hodgkin, *J. Chem. Soc.*, 3686 (1961).

(18) F. P. Boer and J. W. Turley, *J. Amer. Chem. Soc.*, **91**, 1371 (1969).

(19) M. Tanimura, K. Kobori, M. Kashiwagi, and Y. Kinoshita, *Bull. Chem. Soc. Jap.*, **43**, 1962 (1970).

(20) Unpublished work of D. C. Hodgkin, mentioned in ref 3.

We now report the first definitive structural data on examples of a *cis* and a *trans* acyclic aromatic azo dioxide.²² X-Ray analyses are described for crystals of nitrosobenzene dimer and for 2-nitrosobenzoic acid dimer (4). The latter was chosen as we were in-



terested also in the geometry of the carboxyl group and in the possibilities of gas-solid reactions²⁷ involving 4. We also attempted to isolate the other geometric isomer of nitrosobenzene dimer.

Experimental Section

Infrared (ir) spectra were recorded on Perkin-Elmer Models 137, 237-B, and 521 infrared spectrophotometers and were calibrated to the 1601-cm⁻¹ band of polystyrene. Raman spectra were recorded on a SPEX Ramanlab Model RS-2 recording laser (argon-krypton) Raman spectrophotometer. Nuclear magnetic resonance (nmr) spectra were recorded on Varian Associates Models A-60, A-60A, A-56/60, T-60, HR-220, and HA-100 spectrometers. Chemical shifts are reported as δ (ppm) units relative to the internal standard tetramethylsilane unless noted otherwise. Mass spectra were recorded on a Varian MAT CH5 mass spectrometer by Mr. J. Wrona. Elemental analyses were determined by Mr. J. Nemeth and his associates.

Capillary melting points were determined on a Büchi melting point apparatus and are corrected. Hot-stage studies were performed on either a Kofler hot stage or a Mettler FP-2 furnace. Differential scanning calorimetric (dsc) thermograms were recorded with a DuPont Model 900 thermal analyzer equipped with a dsc module.

Interfacial angles were measured with a Tecam two-circle optical goniometer. Angles between faces were calculated with a program provided by Dr. D. B. Pendergrass, Jr., for the Hewlett-Packard 9100A calculator or with the program GONO (S. R. Byrn, Ph.D. Thesis, University of Illinois, Urbana, 1971).

The absolute ethanol (U. S. Industrial Chemicals Co., USP grade) used in the recrystallizations was purified by distillation three times through a 24-in. column which had been packed with glass helices. The purified ethanol was stored under an atmosphere of nitrogen and removed immediately prior to use.

Thin layer chromatograms (tlc) were accomplished on Eastman Chromatogram sheets which contained a fluorescent indicator. All gas-liquid phase chromatography was performed on a Varian Model A-90P gas chromatograph using an 18-in. column of 15% DC-710 on Chromosorb Q.

Preparation and Purification of Nitrosobenzene Dimer. As the material available commercially was of unacceptable quality, nitrosobenzene was prepared by the method of Coleman, McCloskey,

(21) Y. Hanyu and J. E. Boggs, *J. Chem. Phys.*, **43**, 3454 (1965); Y. Hanyu, C. O. Britt, and J. E. Boggs, *ibid.*, **45**, 4725 (1966).

(22) X-Ray data have been obtained on the monomers of *N,N*-dimethyl-4-nitrosoaniline,²³ *N,N*-dimethyl-3-iodo-4-nitrosoaniline,²⁴ and 2,6-diiodo-4-methylnitrosobenzene.²⁴ Results have also been published on the cyclic *cis*-azo dioxide, 1,8-dinitrosonaphthalene,²⁵ and on several 1,2-dinitroso derivatives that exist in the benzofuroxan structure.²⁶

(23) C. Rømming and H. J. Talberg, *Acta Chem. Scand.*, **27**, 2246 (1973).

(24) N. N. Thayer and I. C. Paul, unpublished data.

(25) C. K. Prout, T. S. Cameron, R. M. A. Dunn, O. J. R. Hodder, and D. Viterbo, *Acta Crystallogr., Sect. B*, **27**, 1310 (1971).

(26) See, for example, H. H. Cady, A. C. Larsen, and D. T. Cromer, *Acta Crystallogr.*, **20**, 336 (1966); D. Britton and W. E. Noland, *J. Org. Chem.*, **27**, 3218 (1962); R. C. Gehr and D. Britton, *Acta Crystallogr., Sect. B*, **28**, 1126 (1972); D. Britton, G. L. Hardgrove, R. Hegstrom, and G. V. Nelson, *ibid.*, **1121** (1972); T. S. Cameron and C. K. Prout, *Chem. Commun.*, 684 (1968).

(27) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **96**, 6329 (1974), and references cited therein; I. C. Paul and D. Y. Curtin, *Science*, in press.

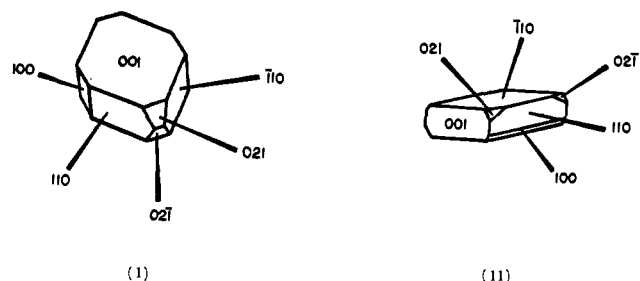


Figure 1. Two habits of the crystals of *cis*-azobenzene dioxide (3a) with faces indexed.

and Stuart.²⁹ The calculated overall yield based on starting nitrobenzene was 68%. Nitrosobenzene dimer was purified by repeated recrystallization from degassed absolute ethanol. The colorless crystals of the dimer dissolved slowly in ethanol at room temperature to give a blue solution. Crystallization was induced by cooling the solution, stored under a nitrogen atmosphere, to -18° . The period of crystallization varied from 5 days to 3 months. The resultant well-formed crystals were colorless and existed in two morphologically distinct crystalline forms: ir (KBr) 1400; (Nujol mull) 1395; (Fluorolube mull) 1395 cm^{-1} ²⁹ (broad, *cis*-nitroso dimer); ir (CCl_4) 1505 (nitroso monomer), 1435 and 1425 cm^{-1} (aromatic ring modes); mass spectrum (70 eV) *m/e* (relative intensity) 107 (76), 77 (100), 51 (75), and 50 (27); Raman (powder) 1602, 1419, and 1268 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 67.23; H, 4.70; N, 13.14. Found: C, 67.01; H, 4.66; N, 13.22.

When heated in a capillary melting-point apparatus, colorless crystals of nitrosobenzene dimer displayed a visually detectable green coloration at 67.1° , began to collapse to a green melt at 68.3° , and melted completely at 68.9° . When colorless crystals of nitrosobenzene dimer were heated on a Kofler hot stage and observed carefully through a microscope, green coloration was detectable at temperatures as low as 50° ; the melting point range was dependent upon the rate of heating.

The proton nmr spectrum of nitrosobenzene is solvent dependent. The width of the complex aromatic multiplet varies approximately from 0.6 in carbon tetrachloride to 0.3 ppm in acetone- d_6 .

Crystallographic Studies of Nitrosobenzene Dimer. The recognition of two habits for nitrosobenzene dimer and the determination of cell dimensions and space group had been reported by Hulme.³⁰ The two habits, with assigned faces, are shown in Figure 1. X-Ray examination reveals that they give the same diffraction pattern. Crystal data: $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ (dimer), $M = 214.36$, orthorhombic, $a = 10.460$ (3), $b = 13.833$ (3), $c = 15.156$ (5) Å; $V = 2193$ (2) Å³; $F(000) = 896$; $\mu(\text{Cu K}\alpha) = 7.54$ cm^{-1} ; $\rho_{\text{measd}} = 1.31$ g cm^{-3} ; $Z = 8$, $\rho_{\text{calcd}} = 1.30$ g cm^{-3} ; systematic absences, $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h + k = 2n + 1$, lead unambiguously to the space group *Pbcn* (No. 60). The symmetry of the space group would impose no constraint upon a dimer molecule. Unit cell parameters were determined by a least-squares refinement of the settings for 12 high-order reflections carefully centered on a Picker FACS-1 diffractometer (λ 1.54184 Å).

Intensity data were collected at ambient temperatures on a small crystal of habit I, with approximate dimensions of $0.2 \times 0.2 \times 0.2$ mm. All unique reflections within the 2θ range of 3 – 130° were

(28) G. H. Coleman, C. H. McCloskey, and F. A. Stuart, "Organic Syntheses," Vol. 25, W. Bachmann, Ed., Wiley, New York, N. Y., 1945, p 80.

(29) In both the KBr disk spectra and, to a lesser extent, in the Nujol mull spectra there were very weak absorptions at ~ 1260 cm^{-1} . These were so weak that we hesitate to consider them to be due to vibrations of the azo dioxide group.

(30) R. Hulme, *Chem. Ind. (London)*, 42 (1962). While the cell data ($a = 10.48$, $b = 13.80$, $c = 15.00$ Å) reported by Hulme are in reasonable agreement with those found in the present study, the indices assigned to some of the faces are not, although the data reported by Hulme are quite limited. There were also earlier morphological studies on nitrosobenzene. There was a study by Haushofer and reported by E. Bamberger and L. Storch, *Chem. Ber.*, 26, 471 (1893), which, although it erroneously reported that the crystals were monoclinic, appears to be consistent with crystals of habit II. Another study by F. M. Jaeger, *Z. Kristallogr.*, 42, 246 (1907), appears to have been made on crystals with a different morphology from those reported herein and which we have been unable to reproduce. See also P. Groth, "Chemische Crystallographie," Vol. 4, Englemann, Leipzig, 1917, pp 10–11.

measured using a moving-crystal, moving-counter technique at a scan rate of $2^{\circ} \text{min}^{-1}$. Three standard reflections were measured every 25 reflections. Although severe cracking was observed in the crystal, the sum of the net intensities for the three standard reflections varied randomly $\pm 2\%$ throughout the period of data collection. The general procedures for data collection have been described previously.³¹ A total of 1084 reflections out of 2160 measured independent reflections was considered observed at the 2σ level. No corrections for absorption or extinction were employed.

The structure was solved by the symbolic addition method, using the FAME, MAGIC, LINK, SYMPL series of programs.³² The hydrogen atoms were readily located from a difference electron density map. Full-matrix least-squares refinement, varying positional and anisotropic thermal parameters for the nonhydrogen atoms, and positional and isotropic thermal parameters for the hydrogen atoms, gave, at convergence, a final R value of 0.060 and a weighted R factor (R_2)³³ of 0.048 on all observed reflections. In the refinement the quantity minimized was $\sum w|F_o| - |F_c|^2$ and the reflections were weighted according to the method proposed by Corfield, Doedens, and Ibers.³⁴ The scattering factors of Cromer and Mann³⁵ and of Stewart, Davidson, and Simpson³⁶ were used for the nonhydrogen atoms and hydrogen atoms, respectively. The final values for the atomic coordinates are listed in Table I.³⁷

Table I. Atomic Coordinates for *cis*-Azobenzene Dioxide^a

Atom	x	y	z
N(1)	0.4064 (3)	0.1573 (3)	-0.0316 (2)
N(2)	0.3514 (3)	0.0804 (2)	0.0035 (2)
O(1)	0.4305 (3)	0.1586 (2)	-0.1135 (2)
O(2)	0.3295 (3)	0.0069 (2)	-0.0434 (2)
C(1)	0.4518 (4)	0.2345 (3)	0.0254 (2)
C(2)	0.4023 (5)	0.3258 (3)	0.0142 (3)
C(3)	0.4470 (6)	0.3998 (4)	0.0669 (4)
C(4)	0.5410 (6)	0.3816 (4)	0.1275 (4)
C(5)	0.5912 (5)	0.2906 (4)	0.1373 (3)
C(6)	0.5468 (4)	0.2154 (4)	0.0855 (3)
C(7)	0.3032 (4)	0.0865 (3)	0.0940 (2)
C(8)	0.2124 (4)	0.1540 (3)	0.1139 (3)
C(9)	0.1652 (5)	0.1573 (4)	0.1997 (3)
C(10)	0.2089 (6)	0.0925 (4)	0.2607 (3)
C(11)	0.2987 (6)	0.0242 (4)	0.2392 (3)
C(12)	0.3484 (4)	0.0195 (3)	0.1538 (3)
H(2)	0.337 (4)	0.334 (3)	-0.027 (2)
H(3)	0.413 (4)	0.466 (3)	0.062 (3)
H(4)	0.572 (5)	0.437 (3)	0.169 (3)
H(5)	0.662 (4)	0.281 (3)	0.180 (3)
H(6)	0.576 (4)	0.146 (3)	0.095 (2)
H(8)	0.185 (4)	0.199 (3)	0.073 (2)
H(9)	0.103 (4)	0.208 (3)	0.216 (3)
H(10)	0.179 (4)	0.092 (3)	0.318 (3)
H(11)	0.331 (4)	-0.019 (3)	0.278 (3)
H(12)	0.427 (4)	-0.029 (3)	0.139 (3)

^a Estimated standard deviations are given in parentheses.

Observation of the Melt of Nitrosobenzene Dimer. Several transparent crystals of nitrosobenzene dimer were ground gently in a mortar and pestle and placed between two NaCl disks. The disks were held together with Teflon tape and heated on a hot plate. When all of the material had melted, the ir (melt, NaCl) showed absorptions at 1495 (nitroso monomer), 1395 (*cis*-nitroso dimer), and a larger absorption at 1260 cm^{-1} (*trans*-nitroso dimer). No significant absorption at 1260 cm^{-1} was observed in any of the following spectra: mull in Nujol of crystalline nitrosobenzene

(31) R. S. Miller, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 96, 6334 (1974).

(32) R. B. K. Dewar, Ph.D. Thesis, University of Chicago, 1969.

(33) $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_2 = [\sum w|F_o| - |F_c|^2 / \sum w|F_o|^2]^{1/2}$.

(34) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(35) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24, 321 (1968).

(36) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(37) See paragraph at end of paper regarding supplementary material.

dimer, a CCl_4 solution of nitrosobenzene, or a CS_2 solution of nitrosobenzene. The ir spectrum was recorded after the melt had solidified: ir (NaCl) 1395 cm^{-1} (broad, *cis*-nitroso dimer). There were no significant absorptions in the spectrum of the resolidified melt to suggest the presence of *trans*-nitroso dimers. The process of melting and resolidification could be repeated several times with no change in the spectra of the two phases being observed.

Preparation of the Dimer of 2-Nitrosobenzoic Acid. The procedure of Heller³⁸ was followed. The yield was 76%. Recrystallization from absolute ethanol at -18° gave a colorless powder, unsuitable for microscopic examination or single-crystal X-Ray crystallographic examination. Suitable pale-yellow crystals were isolated by the slow evaporation of solutions of 2-nitrosobenzoic acid in binary acetone-water solvent systems: mp 225° dec (hot stage); ir (KBr) $1688\text{ (C=O, carboxylic acid)}$, 1298 , 1282 , and 1270 cm^{-1} (broad, *trans*-nitroso dimer); ir (Nujol) 1300 and 1270 cm^{-1} (broad, *trans*-nitroso dimer); mass spectrum (70 eV) *m/e* (relative intensity) 151 (100), 121 (44), 93 (54), 76 (12), 65 (82), 51 (20), 50 (25), 39 (39), and 30 (10). The proton nmr spectrum ($\text{DMSO-}d_6$) was complex, yet consistent with the structure of 2-nitrosobenzoic acid.

The dsc thermogram showed a single endotherm with an extrapolated onset temperature of 228° .

Anal. Calcd for $\text{C}_7\text{H}_7\text{NO}_3$: C, 55.60; H, 3.33; N, 9.31. Found: C, 55.72; H, 3.35; N, 9.25.

Crystallographic Studies of 2-Nitrosobenzoic Acid Dimer. Crystal data: $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_6$, $M = 302.38$, triclinic $a = 7.623$ (4), $b = 7.412$ (4), $c = 6.746$ (4) Å; $\alpha = 115.14$ (4), $\beta = 106.66$ (4), $\gamma = 94.20$ (4) $^\circ$; $V = 302.2$ (9) Å³; $F(000) = 144$; $\mu(\text{Cu K}\alpha) = 10.33\text{ cm}^{-1}$; $\rho_{\text{measd}} = 1.57\text{ g cm}^{-3}$ (floatation in aqueous zinc chloride); $Z = 1$, $\rho_{\text{calcd}} = 1.56\text{ g cm}^{-3}$. The space group is either $P1$ or $P\bar{1}$ (λ 1.54178 Å). If the latter, the molecule is required to have C_2 symmetry.

Intensity data were collected on a small crystal with approximate dimensions of $0.3 \times 0.3 \times 0.3\text{ mm}$. The intensities of all unique reflections within the 2θ range of $3\text{--}130^\circ$ were measured using a moving-crystal, moving-counter technique with a 2θ scan rate of 1° min^{-1} . The intensities of three standard reflections were measured every 50 reflections. Although little change in the appearance of the crystal was noticed during the period of data collection, the average intensity of the three standard reflections dropped 12%. A total of 880 reflections out of 1070 measured reflections was observed at the 4σ level. No corrections for absorption or extinction were applied.

The statistical distribution of normalized structure amplitudes was hypercentric; the space group was considered to be $P\bar{1}$. Attempts to solve the structure by symbolic addition methods were not successful. Examination of the Patterson map revealed the orientation of the phenyl ring. The structure was solved following a suggestion by Byrn.³⁹ The positions of the carbon atoms in the benzene ring were calculated assuming the ring to be positioned at the origin of the unit cell and in the orientation revealed by the Patterson map. A Fourier map phased on these carbon-atom positions was calculated assuming the space group to be $P1$. Several peaks consistent with a *trans*-nitroso dimer were visible. All non-hydrogen atoms in the molecule were positioned by Fourier methods with the space group still considered to be $P1$, although the orientation of the molecule implied C_2 symmetry. The coordinates were then transformed to the $P\bar{1}$ setting, and least-squares refinement commenced. After several cycles the refinement converged and gave an R factor of 0.052 and a weighted R factor of 0.062. A final difference map showed no peaks with an electron density greater than 0.2 e \AA^{-3} . Several negative intensity peaks with densities between -0.3 and -0.4 e \AA^{-3} were observed but appeared to have no chemical significance. Scattering curves were the same as used previously. The final atomic coordinates are listed in Table II.^{37, 40}

(38) G. Heller, *J. Prakt. Chem.*, (2) **106**, 1 (1923).

(39) S. R. Byrn, personal communication, 1971. The method was used subsequently to solve the structure of 4-chlorobenzoic acid.³¹ It was apparently first employed by E. B. Fleischer, *Acta Crystallogr., Sect. A*, **26**, 575 (1970).

(40) The structures of the dimers of both nitrosobenzene and 2-nitrosobenzoic acid were refined initially with unit weights before the weighting scheme based on counting statistics³⁴ was introduced. In the case of the nitrosobenzene dimer the differences in the results were very slight indeed. The overall R factor based on unit weights was slightly lower, 0.057, but R_1 was higher, 0.073. The lengths involving only nonhydrogen atoms did not change very much, although the C-H lengths were more consistent after the refinement using nonunit weights. For 2-

Table II. Atomic Coordinates in Fractional Cell Coordinates for *trans*-2,2'-Dicarboxyazobenzene Dioxide^a

Atom	x	y	z
N	0.4442 (2)	0.4724 (3)	0.5448 (3)
O(1)	0.4157 (3)	0.2942 (2)	0.5259 (3)
O(2)	0.0000 (3)	0.7061 (3)	0.2648 (3)
O(3)	0.1645 (2)	0.4661 (3)	0.1905 (3)
C(1)	0.3651 (3)	0.6304 (3)	0.6864 (4)
C(2)	0.4428 (4)	0.7032 (4)	0.9256 (4)
C(3)	0.3697 (4)	0.8471 (4)	1.0698 (4)
C(4)	0.2230 (4)	0.9168 (4)	0.9764 (4)
C(5)	0.1438 (4)	0.8419 (4)	0.7357 (4)
C(6)	0.2141 (3)	0.6968 (4)	0.5868 (4)
C(7)	0.1253 (3)	0.6126 (4)	0.3286 (4)
H(1)	-0.060 (6)	0.645 (7)	0.103 (8)
H(2)	0.549 (4)	0.653 (4)	0.985 (5)
H(3)	0.420 (4)	0.901 (4)	1.239 (5)
H(4)	0.170 (4)	1.009 (5)	1.065 (5)
H(5)	0.036 (4)	0.891 (4)	0.674 (5)

^a Estimated standard deviations are given in parentheses.

Results and Discussion

The results of the X-ray analysis show that nitrosobenzene exists as the *cis*-azobenzene dioxide structure (**3a**) in the familiar colorless crystals. While the very recent results of Prout and colleagues⁴¹ on the crystals of pentafluoronitrosobenzene show that it is possible for monomeric and dimeric aromatic nitroso compounds to coexist in the crystalline state, there is no evidence in the nitrosobenzene structure for the presence of any species other than **3a** in the crystals. Stereoscopic views of the molecule of **3a** are shown in Figure 2. This result verifies the prediction of Lüttke¹⁰ based on his study of ir spectral data. Crystalline 2-nitrosobenzoic acid is shown to be the *trans*-azobenzene dioxide dimer (**4**). Stereoscopic views are shown in Figure 3. Bond lengths and angles from the *cis*-azobenzene dioxide structure are given in Table III and those for the 2-nitrosobenzoic acid dimer in Table IV.

The Molecule of *cis*-Azobenzene Dioxide (3a**).** As can be seen from Figure 2, the molecule closely approaches C_2 symmetry. As stated by Prout and co-workers,⁴¹ the conformation found for the *cis* dimer of pentafluoronitrosobenzene (**5**) agrees well with that found by us for **3a**. In **3a**, the benzene rings make angles of 112.0 and 64.2° (*i.e.*, 115.8°) with the best plane through the four central carbon and oxygen atoms of the azo dioxide group. In **5**, the corresponding angles (with fluorine atoms included in the best plane calculations for the ring) are 106.1 and 73.4° . In **3a**, the nitrogen atoms deviate significantly (0.037 and 0.040 \AA) from the best planes of the benzene rings to which they are attached; for **5**, the values are 0.133 and 0.143 \AA . The central C(NO)-CNO group in **3a** is very nonplanar (-0.155 to 0.149 \AA), while in **5** the range is from -0.055 to 0.062 \AA . The nature of the nonplanarity in **3a** can be judged from Figure 2c. There is a considerable twist about the N-N bond, coupled with some displacement of nitrogen from the

nitrosobenzoic acid dimer, particular difficulty was encountered in handling the carboxyl hydrogen when the data were given unit weights. It tended to move very close ($\sim 0.5\text{ \AA}$) to the oxygen atom. This problem did not occur when the data were weighted as described in the text. Once again, the dimensions not involving hydrogen atoms did not change significantly. The final values, based on unit weights, of R and R_2 were 0.057 and 0.066.

(41) C. K. Prout, A. Coda, R. A. Forder, and B. Kamenar, *Cryst. Struct. Commun.*, **3**, 39 (1974); see also P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 1853 (1973).

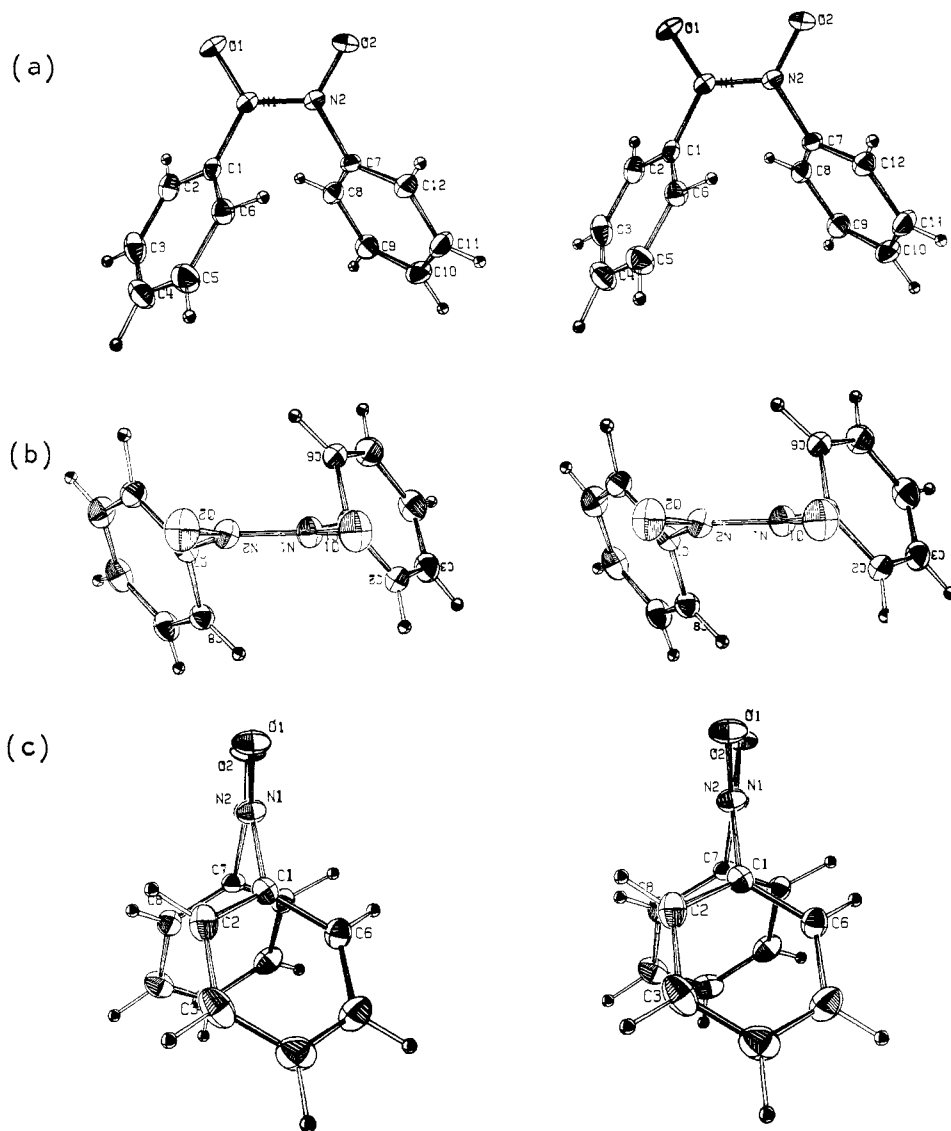


Figure 2. Stereoscopic views of the molecule of *cis*-azobenzene dioxide (**3a**). In (b) and (c) only sufficient atoms labeled to define the numbering system.

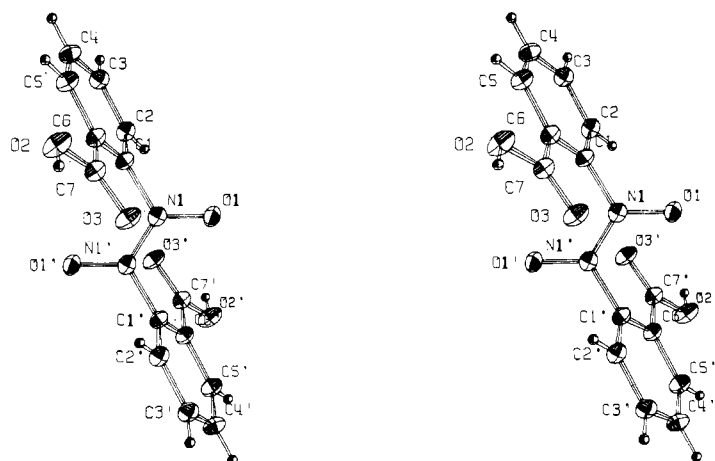


Figure 3. Stereoscopic view of a single molecule of *trans*-2,2'-dicarboxyazobenzene dioxide (**4**).

plane defined by its three bonded neighbors. The C(phenyl)-N-N-C(phenyl) and O-N-N-O torsion angles are 18.0 and 3.9°, respectively, while the out-of-plane distortions at N (1) and N (2) are 0.048 and 0.049 Å,

respectively. In **5**, the corresponding torsion angles are 7.5 and 2.4°, while the out-of-plane distortions are 0.020 and 0.016 Å. Bond lengths and angles will be discussed in the subsequent section.

Table III. Bond Lengths (Å) and Angles (deg) in the *cis*-Azobenzene Dioxide Structure^a

N(1)–N(2)	1.321 (5)	C(5)–C(6)	1.384 (8)
N(1)–O(1)	1.268 (4)	C(1)–C(6)	1.373 (6)
N(2)–O(2)	1.261 (4)	C(7)–C(8)	1.366 (6)
N(1)–C(1)	1.454 (5)	C(8)–C(9)	1.391 (6)
N(2)–C(7)	1.463 (5)	C(9)–C(10)	1.367 (8)
C(1)–C(2)	1.375 (6)	C(10)–C(11)	1.371 (8)
C(2)–C(3)	1.380 (7)	C(11)–C(12)	1.397 (6)
C(3)–C(4)	1.369 (9)	C(7)–C(12)	1.380 (6)
C(4)–C(5)	1.373 (8)		
N(2)–N(1)–O(1)	119.5 (2)	C(4)–C(5)–C(6)	120.0 (4)
N(2)–N(1)–C(1)	119.7 (2)	C(2)–C(1)–C(6)	122.2 (4)
O(1)–N(1)–C(1)	120.4 (2)	C(1)–C(6)–C(5)	118.3 (4)
N(1)–N(2)–O(2)	120.0 (2)	N(2)–C(7)–C(8)	119.1 (2)
N(1)–N(2)–C(7)	118.7 (2)	N(2)–C(7)–C(12)	117.3 (3)
O(2)–N(2)–C(7)	120.8 (3)	C(8)–C(7)–C(12)	123.5 (4)
N(1)–C(1)–C(2)	118.6 (3)	C(7)–C(8)–C(9)	118.3 (3)
N(1)–C(1)–C(6)	119.3 (4)	C(8)–C(9)–C(10)	119.4 (3)
C(1)–C(2)–C(3)	118.8 (3)	C(9)–C(10)–C(11)	121.4 (5)
C(2)–C(3)–C(4)	119.8 (5)	C(10)–C(11)–C(12)	120.4 (4)
C(3)–C(4)–C(5)	121.0 (5)	C(7)–C(12)–C(11)	116.8 (4)

^a The C–H lengths range from 0.91 (4) to 1.09 (4) Å, and the C–C–H angles range from 116 (3) to 123 (2)°.

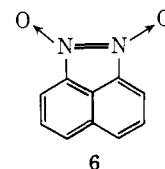
Table IV. Bond Lengths (Å) and Bond Angles (deg) for *trans*-2,2'-Dicarboxyazobenzene Dioxide^{a,b}

N–N'	1.308 (3)	C(5)–C(6)	1.389 (4)
N–O(1)	1.267 (3)	C(1)–C(6)	1.392 (4)
C(1)–N	1.460 (3)	C(6)–C(7)	1.490 (4)
C(1)–C(2)	1.382 (4)	C(7)–O(2)	1.301 (3)
C(2)–C(3)	1.382 (4)	C(7)–O(3)	1.218 (3)
C(3)–C(4)	1.368 (4)	O(2)–H(1)	0.93 (7)
C(4)–C(5)	1.390 (4)		
C(1)–N–N'	117.1 (2)	C(4)–C(5)–C(6)	120.3 (2)
C(1)–N–O(1)	120.5 (2)	C(1)–C(6)–C(5)	118.0 (2)
N'–N–O(1)	122.2 (2)	C(1)–C(6)–C(7)	121.8 (2)
C(2)–C(1)–C(6)	121.8 (2)	C(5)–C(6)–C(7)	120.2 (2)
C(2)–C(1)–N	116.0 (2)	C(6)–C(7)–O(2)	114.1 (2)
C(6)–C(1)–N	112.2 (2)	C(6)–C(7)–O(3)	122.5 (2)
C(1)–C(2)–C(3)	119.1 (2)	O(2)–C(7)–O(3)	123.3 (2)
C(2)–C(3)–C(4)	120.3 (2)	C(7)–O(2)–H(1)	113 (3)
C(3)–C(4)–C(5)	120.6 (2)		

^a The C–H lengths range from 0.90 (4) to 0.98 (3) Å and the C–C–H angles from 116 (2) to 123 (2)°. ^b The atoms designated by primes can be generated from these in this table by 1 – x, 1 – y, and 1 – z.

***trans*-2,2'-Dicarboxyazobenzene Dioxide (4).** This molecule has crystallographic *C_i* symmetry. The nitrogen atom and the carbonyl carbon atom lie 0.052 and 0.050 Å on the same side of the plane of the attached benzene ring. The best plane through the two carbon and two oxygen atoms of the azo dioxide group makes an angle of 73.3° from the best plane through the benzene ring. The best plane through the carboxyl group makes an angle of 8.8° with the plane of the benzene ring. The C–N–N–O torsion angle is 5.5°, and the out-of-plane distortion of nitrogen from its three bonded neighbors is 0.035 Å.

Dimensions of the Azo Dioxide Groups. A detailed comparison of the bond lengths in the azo dioxide groups in the dimers of nitrosobenzene and 2-nitrosobenzoic acid with other nitroso dimers is justified only in the case of the internal *cis* dimer of 1,8-dinitrosophthalene (6),²⁵ the *trans* dimers of 2-nitronitrosoethane¹⁸ and nitrosocyclohexane,¹⁹ and the recently determined structure of the *cis* dimer of pentafluoronitrosobenzene.⁴¹ Structural information for these



nitroso dimers and for some related compounds are given in Table V. The C–N bond lengths in *cis*-azobenzene dioxide and dimeric 2-nitrosobenzoic acid are identical within experimental error and lie intermediate between the values reported in the aliphatic nitroso dimers and in 1,8-dinitrosophthalene. The C–N bond length in *trans*-azoxyanisole⁴² is, however, significantly longer.

The N–N bond lengths in the nitroso dimers are in the range of 1.304–1.321 Å, except for that of the internal dimer of 1,8-dinitrosophthalene which is much longer and must be considered to be almost a single bond. All the N–N bond lengths of the nitroso dimers are significantly longer than the N–N bond lengths observed for *trans*-azoxyanisole,⁴² *trans*-azobenzene,⁴³ and *trans*-*p,p'*-dichloroazobenzene.⁴⁴ The correlation of C–N and N–N bond lengths with bond order has already proved useful in structural descriptions.⁴⁵

The N–O bond lengths for all of the nitroso dimers listed in Table V and for *trans*-azoxyanisole are quite similar and are significantly shorter than the N–O bond lengths in an aliphatic amine oxide (1.409 (10) Å)⁴⁶ or, in what is considered almost a pure N–O single bond, in *O*-picryl ethers (1.441 (5) Å),⁴⁷ but are slightly shorter than those in the aromatic *N*-oxide antibiotics myxin (1.323 (3), 1.288(3) Å)⁴⁸ and iodinin (1.293 (3) Å),⁴⁹ and in a nitroxide (1.291 (7) Å).⁵⁰ The lengths of the N–O nitroso bond in several molecules⁵¹ where the oxygen atom participates in a near-linear X–S···O or X–Se···O interaction are considerably longer (1.312 (6) to 1.365 (9) Å) than those in the present structures. The N–O length in nitroso groups is, however, much longer than those found in nitro groups (1.197 (5) Å).⁵² Unfortunately, there is a lack of reliable data on the N–O lengths in monomeric nitroso compounds. The N–O lengths in the two crystallographically independent molecules of *N,N*-dimethyl-3-iodo-4-nitrosoaniline²⁴ are 1.23 (2) and 1.24 (2) Å, while in the two independent molecules of an aliphatic nitrosocamphane derivative⁵³ they are 1.16 (5) and 1.21 (5) Å. However, more reliable data are required

(42) W. R. Krigbaum, Y. Chatani, and P. G. Barber, *Acta Crystallogr., Sect. B*, **26**, 97 (1970).

(43) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966).

(44) H. Hope and D. Victor, *Acta Crystallogr., Sect. B*, **25**, 1849 (1969).

(45) D. B. Pendergrass, Jr., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **94**, 8730 (1972).

(46) R. L. Muntz, W. H. Pirkle, and I. C. Paul, *J. Chem. Soc., Perkin Trans. 2*, 483 (1972).

(47) J. D. McCullough, Jr., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **94**, 883 (1972).

(48) A. W. Hansen, *Acta Crystallogr., Sect. B*, **24**, 1084 (1968).

(49) A. W. Hansen and K. Huml, *Acta Crystallogr., Sect. B*, **25**, 1766 (1969).

(50) L. J. Berliner, *Acta Crystallogr., Sect. B*, **26**, 1198 (1970).

(51) P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. B*, 946 (1971); E. C. Llaguno and I. C. Paul, *J. Chem. Soc., Perkin Trans. 2*, 2001 (1972); *Tetrahedron Lett.*, 1565 (1973).

(52) The value reported is the average of six N–O lengths in picryl chloride: J. S. Willis, J. M. Stewart, H. L. Ammon, H. S. Preston, R. E. Gluyas, and P. M. Harris, *Acta Crystallogr., Sect. B*, **27**, 786 (1971).

(53) G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1976 (1961).

Table V. Some Data for Dimeric Nitroso Compounds and Structurally Similar Compounds

Compd names	Bond length, Å ^a			Geometry	Ref
	C-N	N-N	N-O		
<i>cis</i> -Azobenzene dioxide	1.454 (5)	1.321 (5)	1.268 (4)	Cis	Present work
(Nitrosobenzene dimer)	1.463 (5)		1.261 (4)		
<i>trans</i> -2,2'-Dicarboxyazobenzene dioxide	1.460 (3)	1.308 (3)	1.267 (3)	Trans	Present work
(2-Nitrosobenzoic acid dimer)					
Perfluoroazobenzene dioxide	1.439 (6)	1.324 (5)	1.267 (6)	Cis	41
(Pentafluoronitrosobenzene dimer)	1.439 (6)		1.267 (6)		
1,8-Dinitrosonaphthalene (Internal dimer)	1.430 (6)	1.376 (5)	1.274 (6)	Cis	25
	1.439 (6)		1.256 (5)		
Nitrosocyclohexane	1.488 (6)	1.319 (6)	1.272 (6)	Trans	19
2-Nitronitrosoethane	1.470 (4) ^b	1.304 (6)	1.262 (4) ^c	Trans	18
Azoxyanisole	1.496 (5)	1.218 (5)	1.279 (4)	Trans	42
Azobenzene ^d	1.433 (3)	1.243 (3)		Trans	43
<i>p,p'</i> -Dichloroazobenzene	1.433 (5)	1.252 (5)		Trans	44

^a Estimated standard deviations are given in parentheses. ^b The C-N bond involving the nitroso group. ^c The N-O bond of the nitroso group. ^d Two unique molecules are present in the unit cell, one of which is disordered. The data presented are from the nondisordered molecule. The estimated standard deviations may be severely underestimated.

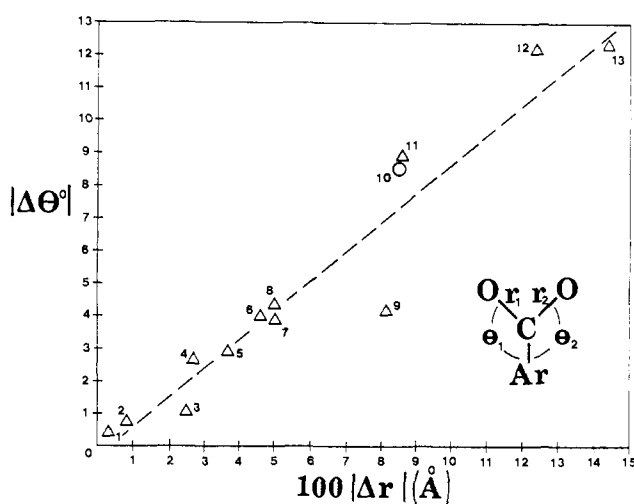


Figure 4. Graphical representation (line drawn by a least-squares fit) of the variation in the differences in bond lengths and bond angles for several aromatic carboxylic acids; (1) 4-methylbenzoic acid [M. G. Takwale and L. M. Pant, *Acta Crystallogr., Sect. B*, **27**, 1152 (1971)]; (2) 4-chlorobenzoic acid [ref 31]; (3) 2-fluorobenzoic acid [J. Krause and H. Dunken, *Acta Crystallogr.*, **20**, 67 (1966)]; (4) 2,4,6-trimethylbenzoic acid [F. Florencio and P. Smith, *ibid.*, *Sect. B*, **26**, 659 (1970)]; (5) 3,4,5-trimethylbenzoic acid [F. H. Cano, S. Martinez-Carrera, and S. Garcia-Blanco, *ibid.*, *Sect. B*, **26**, 972 (1970)]; (6) benzoic acid [G. A. Sim, J. M. Robertson, and T. H. Goodwin, *ibid.*, **8**, 157 (1955)]; (7) 2,6-dimethylbenzoic acid [R. Anca, S. Martinez-Carrera, and S. Garcia-Blanco, *ibid.*, **23**, 1010 (1967)]; (8) pentafluorobenzoic acid [V. Benghiat and L. Leiserowitz, *J. Chem. Soc., Perkin Trans. 2*, 1778 (1972)]; (9) 4-bromobenzoic acid [ref 58]; (10) 2-nitrosobenzoic acid [present work]; (11) 2-chlorobenzoic acid [G. Ferguson and G. A. Sim, *Acta Crystallogr.*, **14**, 1262 (1961)]; (12) 2,3-dimethylbenzoic acid [P. Smith, F. Florencio, and S. Garcia-Blanco, *ibid.*, *Sect. B*, **27**, 2755 (1971)]; (13) 2-bromobenzoic acid [G. Ferguson and G. A. Sim, *ibid.*, **15**, 346 (1962)].

before any conclusion can be drawn about the effect of dimerization on the N-O bond.

The Carboxyl Group. The two carbon-oxygen lengths in the carboxyl group are significantly different, 1.301 (3) and 1.218 (3) Å, with the hydrogen clearly located bonded to O(2). The C-C-O angles are also considerably different; C(6)-C(7)-O(2) is 114.1 (2)° while C(6)-C(7)-O(3) is 122.5 (2)°. A survey of aro-

matic carboxylic acid structures reveals a wide spectrum of values for the C-O lengths and C-C-O angles, ranging from cases where, despite a precise X-ray analysis, the C-O lengths and C-C-O angles are essentially equal, to examples where, as with nitrosobenzoic acid, there is a clear distinction between the single and double bonds, and the C-C-O angle to the double-bonded oxygen is greater than that to the single-bonded oxygen atom. Dunitz and Strickler⁵⁴ appear to have been the first to attribute the equality of C-O lengths in aromatic carboxylic acids to twofold crystallographic disorder. There is a good linear correlation between Δr , the difference in length between the two C-O lengths, and $\Delta\theta$, the difference between the two C-C-O angles (Figure 4). This correlation suggests that disorder occurs in the cases where Δr and $\Delta\theta$ are close to zero. Disorder of the carboxylic acid group was recognized in several carboxylic acids by Filippakis, Leiserowitz, Rabinovich, and Schmidt,⁵⁵ and these workers succeeded in treating this disorder by including "half-hydrogen" atoms in the refinement. However, they did not consider the substantially different positions occupied by the oxygen atoms (due to the difference in the C-O lengths and C-C-O angles) in the two orientations, nor have they pointed out the correlation between the differences in bond lengths and bond angles. A somewhat related correlation among some dicarboxylic acids has been recently proposed by Takusagawa and coworkers.⁵⁶ While many workers have noted the near-equality of C-O lengths in un-ionized carboxylic acids, the explanation that this is a result of disorder in the crystal does not appear to be generally recognized.^{57,58} The proposal for varying amounts of disorder rests on the assumption that either the rate of equilibration between the two forms in the solid state is slow on the laboratory

(54) J. D. Dunitz and P. Strickler in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 595-602.

(55) S. E. Filippakis, L. Leiserowitz, D. Rabinovich, and G. M. J. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1750 (1972).

(56) F. Takusagawa, K. Hirotsu, and A. Shimada, *Bull. Chem. Soc. Jap.*, **46**, 2020 (1973).

(57) M. Simonetta and S. Carra in "The Chemistry of Carboxylic Acids and Esters," S. Patai, Ed., Interscience, London, 1969, pp 1-52.

(58) K. Ohkura, S. Kashino, and M. Haisa, *Bull. Chem. Soc. Jap.*, **45**, 2651 (1972).

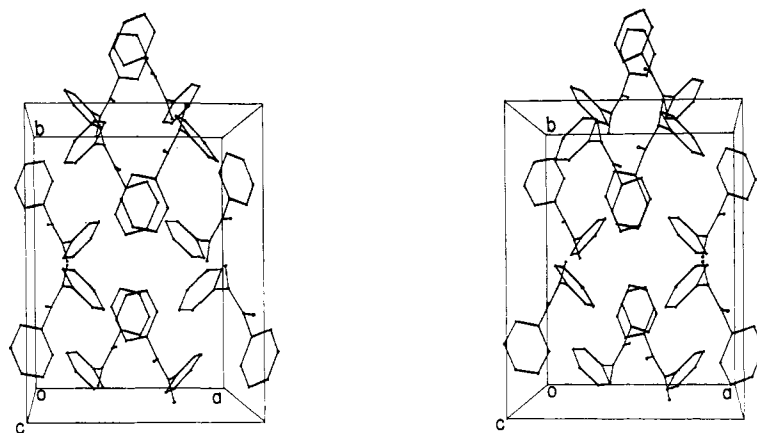


Figure 5. A stereoscopic packing diagram for *cis*-azobenzene dioxide (**3a**). View onto the (001) face. Hydrogen atoms were omitted for clarity.

scale or, should the rate of interconversion be rapid, there must exist a preference for one form over another. From Figure 4 it can be seen that those carboxylic acids singly substituted ortho to the carboxylic acid group tend to be more ordered than those acids substituted para to the carboxyl group. Such data would suggest that should the rate of equilibration be rapid, the ortho substituents perturb the symmetrical potential energy surface for the carboxyl groups sufficiently to cause a significant difference in the populations of both forms. Should the rate of equilibration be slow, these data suggest that ortho substituents preferentially lock the molecule into that form of lowest energy. Although it seems very likely that the rate of proton transfer and subsequent rehybridization would be slow in crystalline carboxylic acids, data concerning the rate of proton transfer in solid acids are not available. From the plot in Figure 4, it can be seen that 2-nitrosobenzoic acid dimer lies well to the ordered side of the continuum of aromatic carboxylic acids.

The carboxyl group participates in a pair of centrosymmetric hydrogen bonds. The O(2)···O(3') distance is 2.619 (3) Å, the H(1)···O(3') distance is 1.69 (7) Å, and the O(2)–H(1)···O(3') angle is 179 (5)°.

Molecular Packing. A stereoscopic view of the crystal packing of *cis*-azobenzene dioxide is shown in Figure 5. The developed faces of the crystal of **3a** can be understood in terms of the molecular packing. Looking down upon the (001) face (Figure 5), the molecular packing is characterized by a quadrilateral arrangement of four molecules of **3a**. These molecules are arranged in pairs; these pairs consist of molecules related by a center of symmetry with N···O distances of 3.61 Å. Distinct cleavage planes parallel to the (110), ($\bar{1}\bar{1}0$), ($\bar{1}10$), and ($1\bar{1}0$) faces are evident; these four faces are prominent in both crystalline habits (Figure 1). The polar azo dioxo groups are oriented along the [001] direction. There is a layer type packing along the [001] direction when viewed from either the (010) or (100) face.

The packing in the crystals of pentafluoronitrosobenzene is quite different from that in *cis*-azobenzene dioxide. In pentafluoronitrosobenzene, the oxygen atoms of the *cis*-azo dioxide group point into the concave space bounded by the two phenyl groups of an adjacent dimer. As the pentafluoronitrosobenzene monomers are completely disordered in the crystal,

there does not appear to be any specific interaction involving the nitroso group of the monomer.

The crystals of dimeric 2-nitrosobenzoic acid exhibit an obvious triclinic external morphology. Unambiguous assignment of crystal faces was difficult owing to close similarities among interfacial angles. However, the development of the set of faces ($12\bar{1}$), (101), and ($10\bar{1}$) could explain the goniometric data and is reasonable in terms of the arrangement of molecules in the crystal (Figure 6). The molecules of **4** form, by hydrogen bonding, infinite chains that run in the [101] direction. These chains form layers parallel to ($12\bar{1}$). The ($10\bar{1}$) face appears to be predominantly nonpolar, while the surface of the (101) face appears to be corrugated with free carboxyl groups projecting from the surface.

When crystals of **4** were heated, they darkened and decomposed at 225°. No green color was evident during heating, and a thermogram exhibited only a single melting endotherm with an onset temperature of 228°.

Detection of the Trans Dimer (3b) of Nitrosobenzene. With the demonstration that the colorless crystals of nitrosobenzene dimer contain only the *cis*-azobenzene dioxide structure (**3a**), there were no data to support existence of the trans dimer (**3b**). It is rather surprising that the presumably more sterically crowded *cis* dimer should be the one to form stable crystals as most other aromatic nitroso compounds appear to crystallize as trans dimers¹⁰ and trans aliphatic nitroso dimers are preferred thermodynamically over the *cis* dimers,⁵⁹ while the trans forms of azobenzene and azoxybenzene are preferred over the *cis* forms.^{60,61} Mullir spectra as well as KBr disk spectra supported the data presented by Lüttke that there were no significant absorptions in the region 1253–1299 cm⁻¹ that might represent trans dimer.²⁹ When crystals were mullied, a blue color appeared and the presence of nitrosobenzene monomer was detected by an absorption at 1505 (Fluorolube mull) and 1510 cm⁻¹ (Nujol mull) (*cf.* 1505 cm⁻¹ in

(59) H. T. J. Chilton, B. G. Gowenlock, and J. Trotman, *Chem. Ind. (London)*, 538 (1955); B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

(60) R. J. W. LeFèvre and J. Northcott, *J. Chem. Soc.*, 867 (1953), and references therein; M. Tsuda and K. Kuratani, *Bull. Chem. Soc. Jap.*, 37, 1284 (1964).

(61) A. Reissert, *Chem. Ber.*, 42, 1364 (1909); P. Luner and C. A. Winkler, *Can. J. Chem.*, 30, 679 (1952).

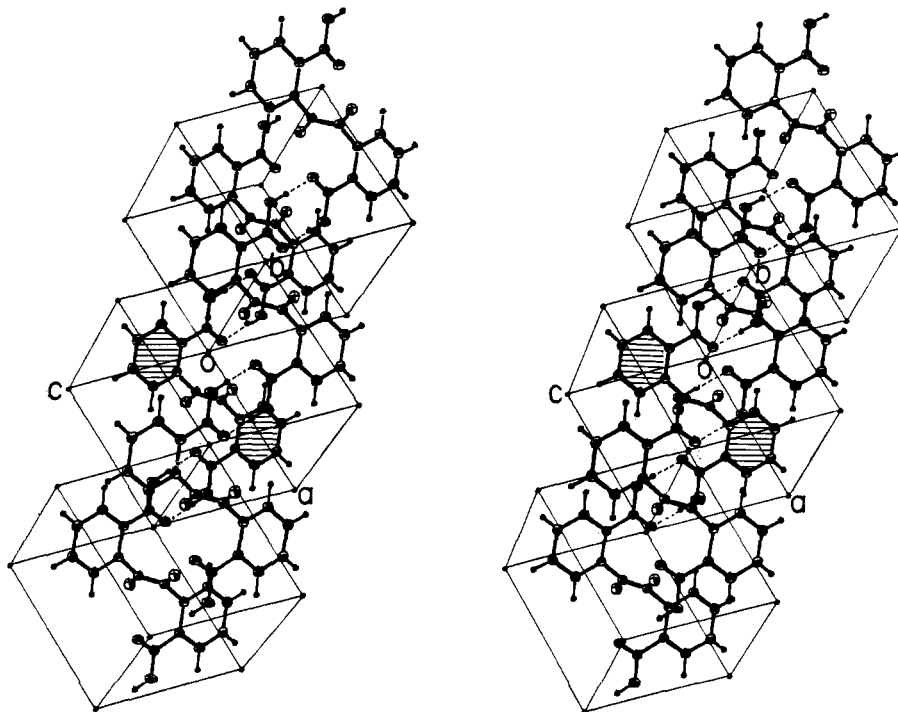


Figure 6. A stereoscopic packing diagram for *trans*-2,2'-dicarboxyazobenzene dioxide (4). Three unit cells are shown. The reference molecule is shaded.

CCl_4 solution). When the crystals were heated, there was no detectable change either visually or by thermograms until melting commenced near 67.1° when a green color appeared.

Evidence for the existence of *trans* dimer was obtained from the melt. Ir spectra of the melt showed the presence of nitrosobenzene monomer, *cis* dimer (1395), and, in greater abundance, *trans* dimer (1260 cm^{-1}). This last absorption is consistent with the absorption reported by Lüttke for other *trans* dimers. Lüttke⁶² had previously determined that nitrobenzene and azoxybenzene were the decomposition products, and they are inconsistent with the 1260-cm^{-1} absorption. It should be noted that in the initial melt spectrum reported by Lüttke,⁶² significant absorptions are detectable, but with lower intensities, in the region of *ca.* 1400 and 1265 cm^{-1} , but no assignment of these bands was made. Crystallization of the melt gives a solid from which absorption due only to *cis* dimer can be detected.

As the ir spectra of the melt suggests the presence of both *cis* and *trans* dimers (3a and 3b), the isolation by crystallization of only the *cis* dimer appears to be related to packing considerations. At present, there are not sufficient data to determine if the *cis* dimer is thermodynamically the more stable form, or if preferential crystallization of the *cis* isomer causes its isolation.

(62) W. Lüttke, *Z. Elektrochem.*, **61**, 302 (1957).

Attempts were made to isolate the *trans* dimer by rapid cooling of the melt. While no definitive results were obtained, there is evidence for a metastable form of nitrosobenzene crystals (apparently previously detected and reported by Schaum⁶³) which exhibit an exotherm at approximately -35° , and the solid-solid interconversion has been followed by photomicrography.⁶⁴ However, efforts to demonstrate that this crystalline form contains the *trans* dimer have not met with success.

Our results provide a firm structural basis for Lüttke's spectroscopic correlation. Accurate values for the lengths and angles in aromatic nitroso dimers have also been obtained. Our work emphasizes the need for an understanding of the role of the solid state in the chemistry of nitroso compounds.

Supplementary Material Available. Tables of anisotropic temperature factors and lists of $h, k, l, |F_o|$, and $|F_c|$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ($105 \times 148\text{ mm}$, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6372.

(63) K. Schaum, *Justus Liebigs Ann. Chem.*, **308**, 18 (1899); K. Schaum, *Z. Kristallogr.*, **35**, 381 (1902).

(64) These and other phenomena involving crystal transformations and defects for nitrosobenzene dimer will be reported elsewhere: D. A. Dieterich, D. Y. Curtin, and I. C. Paul, *Mol. Cryst. Liquid Cryst.*, to be submitted for publication.