# Organic and Biological Chemistry

## The Crystal and Molecular Structure of a *trans*-Nitroso Dimer, $(ONCH_2CH_2NO_2)_2$[1]

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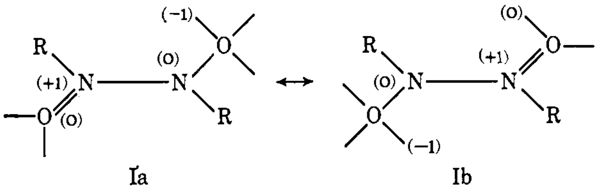
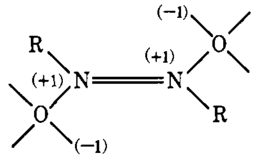
**Abstract:** The reaction product of ethylene and $N_2O_3$ is identified by a three-dimensional, single-crystal X-ray diffraction study as the *trans* dimer of 2-nitronitrosoethane, with dimerization through the nitroso nitrogens at a center of symmetry. The space group is $P2_1/n$, with two molecules in a unit cell of dimensions $a = 8.749$, $b = 9.786$, $c = 4.945$ Å, and $\beta = 95.6°$. The structure was solved by reiterative application of the Sayre equation. The nitroso N–O bond length of 1.262 ± 0.004 Å is considerably shorter than earlier estimates of this distance in C-nitroso dimers. The N–N bond length is 1.304 ± 0.006 Å. The final agreement factor $R_1$ is 10.8% for 610 observed reflections.

Nitroso compounds are a system of considerable theoretical interest, and their dimerization has been the stimulus for some lively discussion in the chemical literature.[2–12] Much attention[2–7] has been focussed on the relative merits of two conventional resonance structures[7]

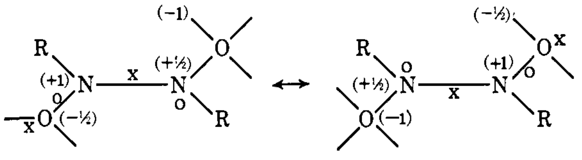


Ia Ib

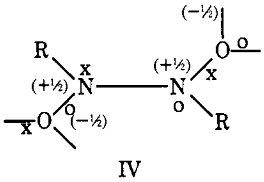


II

and of two additional electronic configurations advocated by Linnett and his coworkers[8–11]

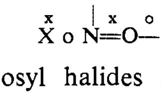


IIIa IIIb



IV

where electrons of opposite spin (denoted by x and o) are permitted to separate in space. The existence of *cis–trans* isomers and the observation that the nitrogen–nitrogen distance is shorter than a single bond have been cited[5,6] as evidence against structure I, whereas the juxtaposition of formal positive charges[9] is an objection to II. Linnett has proposed[8,9] that the reduction of electronic repulsion through spatial separation of electron pairs (III and IV) can account for the fact that alkyl nitroso compounds dimerize readily while nitrosyl halides do not. The electronic structure



$$\overset{x}{X}\;o\;\overset{|\;x}{N}{=}\overset{o}{O}{-}$$

suggested for nitrosyl halides already permits pair separation in the monomer, whereas alkyl nitroso monomers are allowed only the paired structure RN=O<. Thus, dimerization leads to a net gain of energy in the latter case, but not in the former. More simply, Gowenlock and Lüttke[6] have stated that monomers in which the substituent donates electrons to the nitroso group (which is a strong electron acceptor) will not dimerize, whereas electron-accepting substituents will favor the dimer.

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(1) See also F. P. Boer and J. W. Turley, *J. Am. Chem. Soc.*, **89**, 1034 (1967).

(2) D. L. Hammick, *J. Chem. Soc.*, 3105 (1931).

(3) D. L. Hammick, R. G. A. New, and L. E. Sutton, *ibid.*, 742 (1932).

(4) D. L. Hammick, R. G. A. New, and R. B. Williams, *ibid.*, 29 (1934).

(5) J. W. Smith, *ibid.*, 1124 (1957).

(6) B. G. Gowenlock and W. Lüttke, *Quart. Rev.* (London), **12**, 321 (1958).

(7) M. Van Meerssche and G. Leroy, *Bull. Soc. Chim. Belges*, **69**, 492 (1960), estimated by molecular orbital methods that Ia, Ib, and II contribute 24, 24, and 53%, respectively.

(8) J. W. Linnett, "The Electronic Structure of Molecules," Methuen and Co., Ltd., London, 1964, pp 78–82.

(9) J. W. Linnett and R. M. Rosenberg, *Tetrahedron*, **20**, 53 (1964).

(10) J. F. Larcher and J. W. Linnett, *J. Chem. Soc.*, *A*, 1928 (1967).

(11) R. D. Harcourt, *Theoret. Chim. Acta* (Berlin), **3**, 194 (1965).

(12) G. Leroy, M. Van Meerssche, and G. Germain, *J. Chim. Phys.*, **60**, 1282 (1963).

**Table I.** Bond Distances in Nitroso Dimers and Some Monomers[a]

| Structure[b] | $R_1$ | N-N | N-O | N-C | Ref |
|---|---|---|---|---|---|
| 2-Nitronitrosoethane (T) | 0.108 | 1.304 (6) | 1.262 (3) | 1.470 (4) | This work |
| Nitrosoisobutane (T) | 0.111 | 1.27 (2) | 1.30 (2) | 1.51 (2) | 16 |
| Nitrosomethane (C) | 0.156 | 1.31 (2) | 1.31 (2) | 1.47 (3) | 17 |
| Nitrosomethane (T) | 0.115 | 1.22 (4) | 1.25 (2) | 1.57 (8) | 15 |
| *p*-Bromonitrosobenzene (T) |  | 1.31 (5) | 1.35 (5) | 1.40 (5) | 13 |
| 2,4,6-Tribromonitrosobenzene (T) |  | No distances given |  |  | 14 |
| Potassium dinitroso sulfite |  | 1.30 (6) | 1.35 (6) |  | *c* |
| Potassium *syn*-methyl diazotate | 0.084 | 1.246 (8) | 1.306 (7) | 1.477 (10) | *d* |
| *p*-Iodonitrosobenzene (M) | 0.18 |  | 1.24 | 1.28 | *e* |

[a] Estimated standard deviations are shown in parentheses. [b] (T) *trans* dimer, (C) *cis* dimer, (M) monomer. [c] E. G. Cox, G. A. Jeffrey, and H. P. Stadler, *J. Chem. Soc.*, 1783 (1949). [d] Von R. Huber, R. Langer, and W. Hoppe, *Acta Cryst.*, **18**, 467 (1965). [e] M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

For various reasons, earlier attempts to determine the structural parameters of C-nitroso dimers were carried out under conditions not conducive to accurate results. As a result, a wide range of bond lengths (Table I) has been reported: 1.22-1.31 Å for the N-N bond, and 1.25-1.35 for N-O. The two earliest studies, of the 2,4,6-tribromonitrosobenzene[13] and the *p*-bromonitrosobenzene[14] dimers, were seriously limited by the use of two-dimensional projections and the presence of heavy Br atoms. In the former structure, no bond lengths were even reported. Because the crystal structure of the *trans* dimer of nitrosomethane[15] turned out to be disordered, the bond distances in that study had very high standard deviations. All the crystals examined in the X-ray study[16] of *trans*-nitrosoisobutane dimer were twinned; overlapping of reflections from the twinned components prevented a full three-dimensional study and the structure was solved using three projections. More satisfactory conditions seem to have been encountered in the structure of the *cis* dimer of nitrosomethane;[17] a three-dimensional data set was refined to a discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.156$ assuming isotropic temperature factors for the C, N, and O atoms. In view of the emphasis given to experimental bond lengths by the theoretical chemists who have discussed this system,[5-12] a redetermination of the molecular parameters has been urged.[9] In the present study of *trans*-2-nitronitrosoethane dimer, bond distances of 1.304 ± 0.006 Å for N-N and 1.262 ± 0.004 Å for N-O were obtained. The latter result suggests that the generally accepted values (1.31-1.35 Å) for the N-O bond are much too long, and seems to be much more consistent with the observed infrared stretching frequency of 1290 cm$^{-1}$ in C-nitroso dimers.[6]

## Experimental Section

The first reported preparation of 2-nitronitrosoethane dimer appears to be that of Siderenko,[18] who precipitated the substance by passing ethylene gas and "oxides of nitrogen" through ether. In the present preparation, stoichiometric proportions of NO and $O_2$ were bubbled into methylene chloride to produce an $N_2O_3$ solution. Ethylene gas passed through this solution produced transparent crystals of 2-nitronitrosoethane dimer together with an oily material of probable composition $(O_2NCHCH_2)_n$. The same crystalline product was obtained over reaction temperatures ranging from −80 to to 25°. The crystals are needle shaped, decompose without melting at 112°, and have extremely limited solubility in common laboratory solvents. The molecular weight determined by boiling point elevation in methyl ethyl ketone (40 mg/20 g of solvent) is 116 ± 2.6 and indicates the formation of monomer in solution. Although the extreme dilution of the solutions prevents a definitive assignment, nmr spectra recorded at room temperature in methylene chloride and in nitromethane each revealed a lone singlet at $\delta$ 4.9 ppm, suggesting that the protons of the monomer are magnetically, and perhaps also chemically, equivalent. Single-crystal X-ray diffraction data taken on a Weissenberg goniometer with Ni-filtered Cu K$\alpha$ radiation (1.5418 Å) show a reciprocal lattice symmetry $C_{2h}$, with extinctions of $h0l$ for $h + l$ odd and $0k0$ for $k$ odd, establishing space group $P2_1/n$. Unit cell dimensions of $a = 8.749 \pm 0.013$, $b = 9.786 \pm 0.015$, and $c = 4.945 \pm 0.005$ Å and $\beta = 95.6 \pm 0.5°$ were measured giving a calculated crystal density of 1.640 g/cm$^3$ for four monomer units per cell, in good agreement with the observed value of 1.627 g/cm$^3$ measured by flotation. Multiple-film methods were used to collect intensity data for levels $hkL$, $0 \leqslant L \leqslant 3$, and for levels $hKl$, $0 \leqslant K \leqslant 5$, and intensities were estimated visually by comparison with a scale prepared by making known exposures of a reflection from the same crystal.

The intensities were corrected for Lorentz and polarization effects, but absorption effects were neglected in view of the small crystal size and the low linear absorption coefficient of 13.8 cm$^{-1}$ for Cu K$\alpha$ radiation. An initial correlation of the levels was performed using the program DIFCOR,[19] assuming $\sigma(F^2) = 0.10F^2$ for each independent intensity measurement. For reflections measured on both axes, an average $\bar{F}^2 = \sqrt{F_1{}^2F_2{}^2}$ was calculated, with $\sigma(\bar{F}^2)$ taken as $(1/\sqrt{2})(0.10\bar{F}^2)$ if $F_1{}^2$ and $F_2{}^2$ agreed within $0.30\bar{F}^2$, and $\sqrt{2}(0.10\bar{F}^2)$ if they did not. These $\sigma$'s were used to compute the weights $w = 4F^2/\sigma^2(F^2)$ used in the least-squares refinement, where the quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized. (The weighted reliability factor used below is defined by $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.) The correlation showed three reflections (521, 71$\bar{3}$, and 720) with very bad internal agreement and these were omitted from the data set.

## Structure Determination and Refinement

Initial scale and temperature factors were estimated by Wilson's method, and a set of normalized structure factors[20]

$$E_{\vec{h}} = F_{\vec{h}}/\epsilon\left[\sum_{j=1}^{n} f_{j\vec{h}}{}^2\right]^{1/2}$$

were calculated for the three-dimensional set of intensities. The signs of the 74 reflections for which $|E| \geq 1.5$ were determined using the multiple-solution

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

(14) C. P. Fenimore, *J. Am. Chem. Soc.*, **72**, 3226 (1950).

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

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

(17) G. Germain, P. Piret, and M. Van Meerssche, *Acta Cryst.*, **16**, 109 (1963).

(18) (a) J. L. Riebsomer, *Chem. Rev.*, **36**, 157 (1945); (b) K. Siderenko, *J. Russ. Phys. Chem. Soc.*, **45**, 1585 (1913).

(19) DIFCOR is a computer program written for the IBM 7094 by J. A. Hartsuck of the Harvard University Chemistry Department to correlate multilevel intensity data.

(20) Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201-209.

computer program of Long,[21a] which solves the phase problem by reiterative application of Sayre's equation[22]

$$s(E_a) = s\left(\sum_{a=b+c} E_bE_c\right)$$

where s means [‘sign of,” and *a*, *b*, *c* are the vectors (*hkl*) for the reflections a, b, c. The correct solution, which assumed positive signs for $21\bar{1}$, 132, $61\bar{2}$, 310, and 321, and negative signs for $38\bar{3}$ and $19\bar{2}$, gave a consistency index

$$C = \frac{\left\langle \left| E_a \sum_{a=b+c} E_bE_c \right| \right\rangle}{\left\langle |E_a| \sum_{a=b+c} |E_b||E_c| \right\rangle} = 0.97$$

after nine cycles. The seven C, N, and O atoms were found unambiguously from an E map calculated[21b] with these 74 signs, and all the signs were subsequently shown to be determined correctly.

After appropriate atomic scattering factors[20] had been assigned on chemical grounds, five cycles of full-matrix, least-squares refinement[21c] of the atomic positions and isotropic temperature factors reduced $R_1$ from 0.36 to 0.25. An electron density map from which the C, N, and O atoms were subtracted showed four peaks which could reasonably be assigned to the hydrogens. Before proceeding, however, we omitted four intense low-order reflections (101, $21\bar{1}$, $30\bar{1}$, and 301) from the data set because of severe extinction. Four cycles of isotropic refinement on all eleven atoms now reduced $R_1$ to 0.20, and after anisotropic thermal parameters were introduced for the C, N, and O atoms, four additional cycles[1] gave $R_1$ = 0.135. A check on the internal correlation of the data showed a need for rescaling, which was performed by hand with retention of the original weights. Four cycles of additional refinement, varying all position parameters, C, N, and O anisotropic thermal parameters, and H isotropic temperature factors, gave the final discrepancy indices of $R_1$ = 0.108 and $R_2$ = 0.113.[23] The average *x*, *y*, *z* parameter shift for the seven heavy atoms was $0.001\sigma$ in the final cycle, with a maximum shift of $0.006\sigma$. For hydrogen, the average shift was $0.006\sigma$. Table II lists the final atomic parameters and their standard deviations, while Table III gives root-mean-square com-

**Table II.** Final Atomic Parameters[a]

| Atom | *x/a* | *y/b* | *z/c* | Anisotropic thermal parameters[b] $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0.34861 (64) | 0.05737 (42) | 0.73206 (88) | 0.03707 (107) | 0.01179 (44) | 0.06840 (239) | 0.00423 (58) | 0.01355 (121) | 0.01229 (89) |
| O(2) | 0.23721 (36) | 0.24906 (37) | 0.72739 (66) | 0.01261 (45) | 0.01597 (47) | 0.04700 (161) | 0.00009 (38) | 0.00636 (67) | −0.00462 (71) |
| O(3) | 0.55703 (30) | 0.38090 (28) | 0.73720 (51) | 0.01207 (40) | 0.00926 (33) | 0.02864 (117) | 0.00001 (28) | −0.00461 (53) | 0.00392 (49) |
| N(1) | 0.32384 (40) | 0.16973 (37) | 0.63836 (70) | 0.01258 (51) | 0.00940 (40) | 0.03318 (152) | −0.00174 (38) | 0.00238 (68) | −0.00223 (68) |
| N(2) | 0.49172 (34) | 0.43514 (32) | 0.52495 (57) | 0.00893 (39) | 0.00774 (32) | 0.02608 (128) | −0.00041 (30) | −0.00088 (56) | 0.00121 (60) |
| C(1) | 0.39973 (52) | 0.20559 (43) | 0.39196 (85) | 0.01190 (58) | 0.00809 (44) | 0.03380 (181) | −0.00115 (40) | 0.00319 (81) | −0.00287 (77) |
| C(2) | 0.39012 (48) | 0.35588 (42) | 0.32939 (82) | 0.01143 (56) | 0.00887 (47) | 0.02876 (168) | −0.00141 (40 | −0.00280 (76) | −0.00203 (71) |
| H(1) | 0.4980 (65) | 0.1786 (58) | 0.4159 (103) | 5.121 (1190) B[c] | | | | | |
| H(2) | 0.3430 (44) | 0.1516 (41) | 0.2485 (83) | 2.556 (750) | | | | | |
| H(3) | 0.4280 (56) | 0.3710 (51) | 0.1569 (114) | 4.848 (1107) | | | | | |
| H(4) | 0.2922 (42) | 0.3953 (44) | 0.3428 (90) | 3.763 (971) | | | | | |

[a] Numbers in parentheses are estimated standard deviations from the least-squares refinement × $10^5$, for C, N, O; × $10^4$ for H; and × $10^3$ for B(H). [b] Defined by the expression $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. [c] Isotropic thermal parameters.

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(21) Computers and programs used are as follows: (a) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1965; (b) J. Gvildys, "Two- and Three-Dimensional Crystallographic Fourier Summation Program," based on MIFRI, Program Library B-149, Argonne National Laboratory, Applied Mathematics Division, April 13, 1965; (c) J. Gvildys, "A Fortran Crystallographic Least-Squares Refinement Program," based on ORFLS, Program Library 14E7043, Argonne National Laboratory, March 31, 1967; (d) C. K. Johnson, "OR TEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965; (e) J. Gvildys, "ANL FFE, A Fortran Crystallographic Function and Error Program," based on ORFFE, Program Library B-115, Argonne National Laboratory, Sept 17, 1964; (f) J. Gvildys, "Least-Squares Plane and Line Fitter," see V. Shomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 12, 600 (1959), Program Library B-125, Argonne National Laboratory, May 18, 1965.

(22) D. Sayre, *Acta Cryst.*, 5, 60 (1952).

(23) A table of observed and calculated structure factors has been deposited as Document No. NAPS-00166 with the ASIS National Auxiliary Publication Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

**Table III.** Root-Mean-Square Thermal Displacements[a] Along Principal Axes (Å)

| Atom | Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|
| O(1) | 0.195 (5) | 0.299 (5) | 0.391 (5) |
| O(2) | 0.202 (4) | 0.242 (4) | 0.288 (4) |
| O(3) | 0.155 (4) | 0.213 (4) | 0.246 (4) |
| N(1) | 0.191 (5) | 0.208 (4) | 0.236 (4) |
| N(2) | 0.168 (4) | 0.187 (4) | 0.205 (4) |
| C(1) | 0.183 (6) | 0.203 (5) | 0.226 (5) |
| C(2) | 0.163 (5) | 0.212 (5) | 0.231 (5) |
| H(1) | 0.255 (30) | ... | ... |
| H(2) | 0.180 (27) | ... | ... |
| H(3) | 0.248 (29) | ... | ... |
| H(4) | 0.218 (29) | ... | ... |

[a] Estimated standard deviations, × $10^3$, are shown in parentheses.

ponents of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters. The directions of these axes may be inferred from the computer-produced stereo view[21d] of the molecule (Figure 1), where the thermal motion is represented by 50% probability ellipsoids. Table IV gives bond distances and angles with their estimated standard deviations as calculated[21e] from the variance–covariance matrix of the final least-squares cycle.

**Table IV.** Distances and Angles[a]

| Bond | Distance, A | Bond angle | Degrees |
|---|---|---|---|
| | Intramolecular | | |
| N(1)–O(1) | 1.205 (5) | O(3)–N(2)–C(2) | 121.38 (30) |
| N(1)–O(2) | 1.198 (4) | N(2)′–N(2)–O(3) | 121.14 (35) |
| N(2)–O(3) | 1.262 (4) | N(2)′–N(2)–C(2) | 117.43 (41) |
| C(1)–N(1) | 1.485 (5) | | |
| C(1)–C(2) | 1.504 (5) | N(2)–C(2)–C(1) | 111.30 (31) |
| C(2)–N(2) | 1.470 (4) | N(2)–C(2)–H(3) | 105.47 (289) |
| N(2)–N(2)′ | 1.304 (6) | N(2)–C(2)–H(4) | 103.37 (258) |
| | | H(3)–C(2)–H(4) | 113.02 (385) |
| C(1)–H(1) | 0.890 (52) | C(1)–C(2)–H(3) | 108.56 (288) |
| C(1)–H(2) | 0.981 (40) | C(1)–C(2)–H(4) | 114.68 (251) |
| C(2)–H(3) | 0.955 (52) | | |
| C(2)–H(4) | 0.953 (43) | C(2)–C(1)–N(1) | 112.30 (32) |
| | | C(2)–C(1)–H(1) | 110.29 (348) |
| | | C(2)–C(1)–H(2) | 111.34 (212) |
| | | H(1)–C(1)–H(2) | 110.23 (392) |
| | | N(1)–C(1)–H(1) | 108.94 (323) |
| Contact | | N(1)–C(1)–H(2) | 103.54 (216) |
| N(2)–N(1) | 3.063 (4) | | |
| N(2)–O(2) | 3.117 (4) | O(1)–N(1)–O(2) | 123.18 (38) |
| O(3)–N(1) | 2.912 (4) | O(1)–N(1)–C(1) | 116.90 (37) |
| O(3)–O(1) | 3.652 (5) | O(2)–N(1)–C(1) | 119.84 (34) |
| O(3)–O(2) | 3.077 (4) | | |
| C(1)–O(3) | 2.701 (5) | C(1)–N(2)′ | 3.655 (5) |
| C(2)–O(1) | 3.574 (5) | C(1)–O(1)′ | 3.480 (6) |
| C(2)–O(2) | 2.696 (5) | O(3)–O(3)′ | 3.387 (5) |
| C(2)–O(3)′ | 2.643 (5) | O(3)–C(2)′ | 2.643 (5) |
| C(2)–C(2)′ | 3.724 (7) | | |

[a] Single, double, and triple primed atoms designate a symmetry related atom: ′ related by a center of symmetry. Standard deviations given in parentheses were obtained from the variance–covariance matrix calculated during the final least-squares refinement.

## Discussion

The three-dimensional view of the molecular structure (Figure 1) shows that the dimer takes a *trans* configuration with a center of symmetry at the midpoint of the N–N bond. The carbon atoms are staggered, with the projection of the C(1)–N(1) (nitro) bond roughly bisecting the angle between the C(2)–H(4) and C(2)–N(2) (nitroso) bonds. This conformation is evidently stabilized by intramolecular attractive forces, such as those between the negatively polarized nitro oxygen atom O(2) and the positively charged nitroso nitrogen N(3) and a similar interaction between N(1) and O(3). The intramolecular contacts between the nitro and nitroso groups are fairly close: N(2) is 3.117 Å from O(2) and 3.063 Å from N(1), while O(3) is 2.912 Å from N(1), 3.077 Å from O(2), and 3.652 Å from O(1). The plane of the atoms O(3), N(2), N(2)′, and C(2) ($-7.33x + 2.14y + 2.87z = -1.153$), forms a dihedral angle of 102.8° with the plane of C(1), N(1), O(1), and O(2) ($6.26x + 3.70y + 2.55z = 4.264$).[21f] The maximum deviation from the former plane is 0.016 Å (N(1)), and from the latter 0.010 Å (N(2)).

As mentioned previously, a meaningful comparison of bond lengths with earlier structures is difficult because of the large experimental errors there. Our N–N distance of 1.304 ± 0.006 Å agrees with the values reported for *cis*-nitrosomethane (1.31 Å),[17] *p*-bromonitrosobenzene (1.31 Å),[13] and potassium dinitroso sulfite (1.30 Å).[24] It is considerably shorter than the value of 1.41 Å reported[25] for the single bond in $N_2H_6^{2+}$, where adjacent nitrogen atoms may also be expected to bear large positive charges, and thus may reflect substantial double bond character derived from valence structures like II. The only N–O distance from a dimer close to the value reported here, 1.262 ± 0.004 Å, is that for *trans*-nitrosomethane (1.25 Å).[15] The carbon-nitrogen bonds C(1)–N(1) = 1.485 ± 0.005 Å and C(2)–N(2) = 1.470 ± 0.004 Å are in good agreement with established values[25] for 3-covalent nitrogen. The C(1)–C(2) distance, 1.504 ± 0.005 Å, is apparently shortened slightly from the value (1.537 Å)[25] accepted for a single bond between ordinary $sp^3$ carbons. The bond angles at carbon are essentially tetrahedral, while those at the nitro and nitroso nitrogens are not significantly differ-

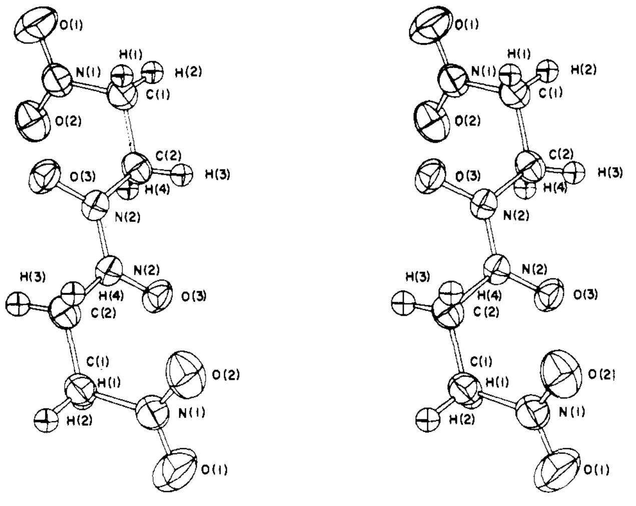

Figure 1. Stereo view of the molecular structure of 2-nitronitrosoethane dimer. Hydrogen atoms are shown as spheres of arbitrary size; all other atoms are shown as ellipsoids of thermal motion.

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(24) See Table I, footnote *c*.

(25) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 18, The Chemical Society, London, 1965, pp S7s, S19s, S14s, S15s.

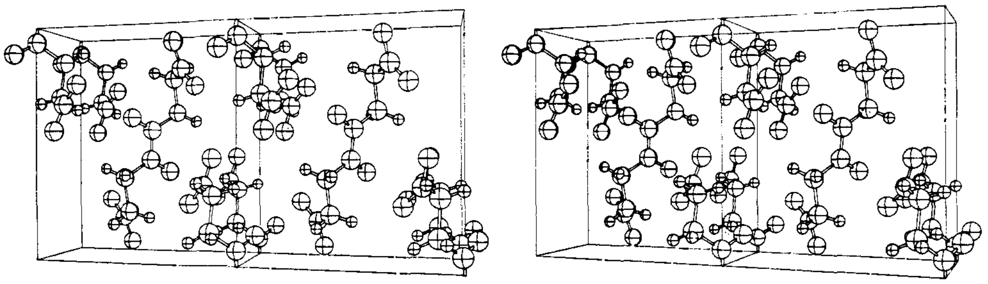

Figure 2. Stereo view of the molecular packing in crystalline 2-nitronitrosoethane dimer with the smaller spheres representing hydrogen atoms. The $y$ axis is vertical and $x$ is horizontal.

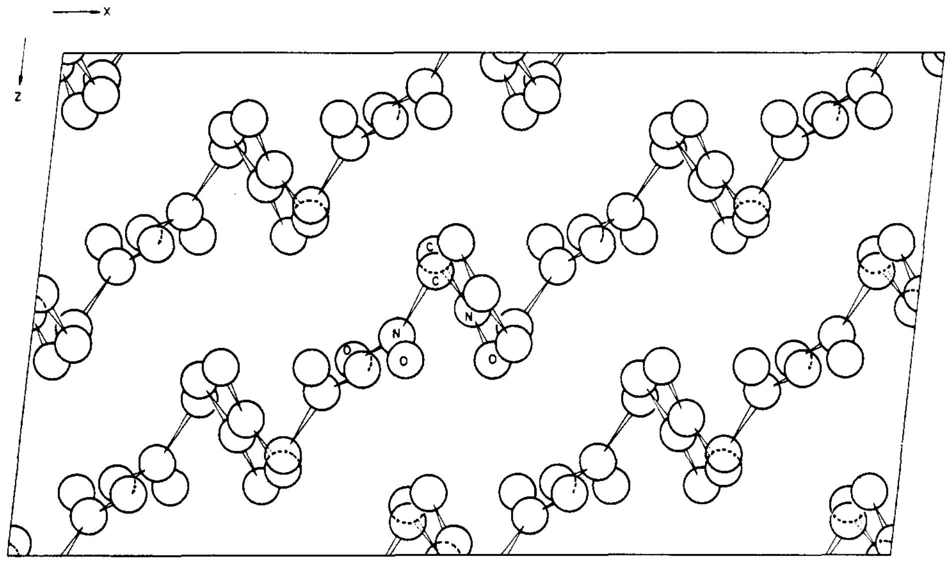

Figure 3. Schematic drawing of the (010) projection of the molecular packing in crystalline 2-nitronitrosoethane. Four unit cells are shown.

ent from the 120° expected for $sp^2$ hybridization. The slight widening of the O(1)-N(1)-O(2) angle to 123.2° has often been observed in structures where the molecular packing is determined by interaction of the nitro group dipoles.[26]

In an earlier communication,[1] we reported a molecular orbital wave function for 2-nitronitrosoethane dimer calculated by a nonempirical method[27,28] that includes all the atoms and electrons of the system. These results appeared to be quite consistent with the experimental N-N and N-O bond distances, and were interpreted[1] to support valence structure II, with some contribution from other structures such as Ia and b acting so as to reduce the formal positive charges on adjacent nitrogens. Wave functions calculated over nonpaired spatial orbitals[10] (which take into account electron correlation) appear to give improved energies, but do not seem necessary to account for the observed bond distances.

The molecular packing, shown in three dimensions in Figure 2 and in a $y$-axis projection in Figure 3, appears to be dominated by dipole–dipole interactions. The strength of these interactions is indicated by the large number of close intermolecular contacts in this structure (see Table IV). The nitro groups are stacked in a direction parallel to the $y$ axis, with their dipoles mutually opposed along 101. The nitroso dipoles, on the other hand, are directed perpendicularly to the nitro dipoles, such that O(3) of one molecule points toward N(1) of another. (The O(3)···N(1) contact distance is 2.954 Å.) Examination of the structure also indicates that the crystal avoids close O···O contacts. The low vapor pressure and insolubility of the compound may be the result of these strong crystal bonding forces.

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[26] For example, see J. W. Turley, *Acta Cryst.*, **B24**, 942 (1968).

[27] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

[28] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *ibid.*, **88**, 2367 (1966).