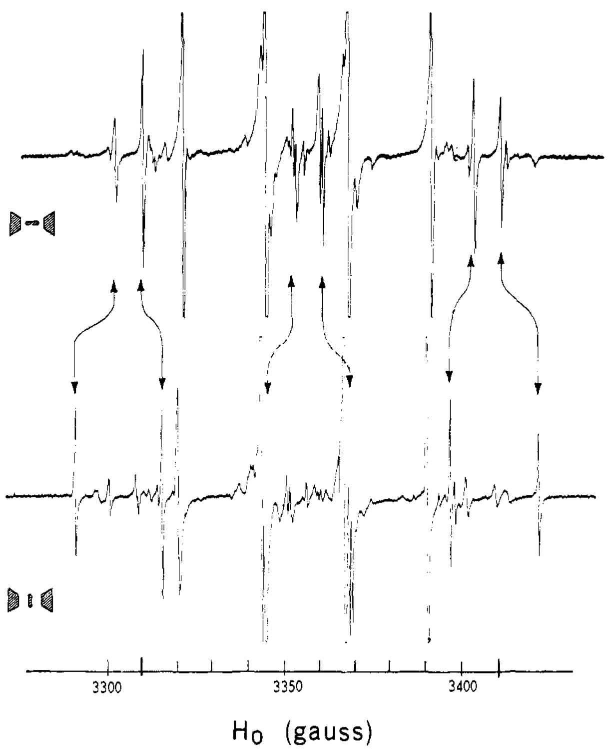


Figure 1. Electron spin resonance spectrum of vinyl (and methyl) radicals trapped in neon for two indicated orientations of the matrix in the magnetic field. Arrows indicate the strong lines identified with vinyl radicals, the remaining stronger lines being due to methyl.

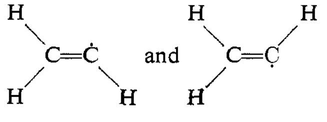
three-spin system with two equivalent members.[4] The observed splittings are given in Table I. By assuming the unique principal axis of the hyperfine tensor to be perpendicular to the surface of the matrix, one derives the isotropic and dipolar couplings also listed in Table I. The isotropic couplings agree closely with the splittings observed in the liquid,[3] substantiating the identity of the radicals. Our failure to observe the expected[5,6] orthorhombic hyperfine tensor makes it necessary to assume motional averaging of two of its components, which most reasonably occurs about the axis of least inertia approximately coincident with the carbon–carbon bond. In-plane rotation of methyl radicals in "soft" matrices has been inferred from relative intensity data,[7,8] and rotation of the molecular plane is evidenced by our failure[9] to observe anisotropy in the ^{13}C splitting of $^{13}CH_3$ radicals trapped in the same way as the vinyl radicals in this experiment. Anomalies in the g values of SiH_3, GeH_3, and SnH_3 have also been interpreted on the basis of rotation.[8]

Table I. Hyperfine Splittings[a] in Trapped Vinyl Radicals

	Doublet	Triplet
I. Observed splittings (Figure 1)		
Perpendicular orientation (top)	7.6	50.5
Parallel orientation (bottom)	24.6	52.5
II. Hyperfine interactions		
Isotropic	13.3	51.5
Dipolar		
Parallel	11.3	1.3
Perpendicular	−5.7	−0.7

[a] In gauss at operating frequency of 9436 MHz.

The spectrum also implies equivalent β-hydrogens. Such equivalence can be easily understood if the α-carbon is linearly hybridized; the odd electron would be in the 2p orbital of the α-carbon directed in the molecular plane perpendicular to the carbon–carbon σ bond. If the α-carbon is trigonally hybridized, however, one must assume that the radical is inverting rapidly ($>10^{10}$ sec^{-1}) between the two equivalent bent configurations



The dipolar parts of the coupling constant to the α-hydrogen shown in Table I are in good agreement with the linear model.[4] However, our results imply that the isotropic coupling to this hydrogen is positive, which is easier to reconcile with a bent structure.[10] It is not possible to distinguish between the two structures on the basis of our experiments. One should note, however, that the observed isotropic coupling to the α-hydrogen has very nearly the same magnitude as that observed in a liquid system for which much slower inversion between the bent configurations (10^7–10^9 sec^{-1}) was proposed in order to account for the absence of the central portion of the expected spectrum.[3]

The implied orientation of vinyl radicals in a neon matrix is opposite from that previously observed for linear molecules such as CuF_2 and bent molecules such as NO_2 and NF_2, where the molecular plane was found to be oriented parallel to the surface.[1,2,11] However, both vanadium oxide and propargyl radicals have since been found to orient, like vinyl, with their axis of least inertia normal to the surface.[9] In the case of vinyl radicals, both the rotation and the apparent lowering of the inversion barrier appear to be associated with the oriented sites, since spectra obtained previously[10] from radicals produced by photolysis of HI in acetylene and argon show none of these characteristics. This suggests that the vinyl radicals in our experiment may be incorporated substitutionally into oriented crystals[12] of neon. We obtain spectra like the original one[10] when argon or krypton is used as a matrix, and in neon vinyl radicals can occupy both types of site to varying extents depending on experimental conditions.

We are making use of the progressive complication of the spectrum in an attempt to analyze it in detail when all motions are frozen out.

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(7) C. K. Jen in "Formation and Trapping of Free Radicals," A. Bass and H. P. Broida, Ed., Academic Press Inc., New York, N. Y., 1960, Chapter 7.
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(11) P. H. Kasai and E. B. Whipple, *Mol. Phys.*, **9**, 497 (1965).
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Paul H. Kasai, Earl B. Whipple
Union Carbide Research Institute
Tarrytown, New York 10591

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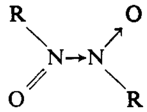
The Molecular Structure of 2-Nitronitrosoethane Dimer

Sir:

The preferred representation of the bonding in C-nitroso dimers has been a subject with a long history of speculation and controversy.[1–7] Two valence struc-

(1) (a) D. L. Hammick, *J. Chem. Soc.*, 3105 (1931); (b) D. L. Ham-



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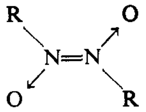

II

tures have been at the center of most recent discussions, although a number of other representations have been suggested.[4] Objections to I have been raised[2,3] largely because of the existence of *cis-trans* isomers and to II because of the juxtaposition of the formal positive charges on the nitrogen atoms.[4,5] Detailed structural investigations have, to be sure, shed some light on this subject, but unfortunately the accuracy of the two published X-ray crystallographic determinations of C-nitroso dimers (2,4,6-tribromonitrosobenzene[6] and *p*-bromonitrosobenzene[7]) is seriously limited by the use of two-dimensional methods and the presence of heavy atoms. In particular, it has been noted[4] that the N–O stretching frequency of 1290 cm^{-1} in nitroso dimers is inconsistent with X-ray estimates of the bond length. We report below a three-dimensional X-ray study of the dimer of 2-nitronitrosoethane, which has in fact yielded some substantially improved values for the lengths of certain bonds and the calculated charge distribution for this species as obtained by molecular orbital methods based on the experimental geometry.

The dimer of 2-nitronitrosoethane was first reported by Siderenko,[8] who obtained it as a precipitate when ethylene and oxides of nitrogen were passed through ether. Crystals of this compound suitable for X-ray analysis were kindly supplied to us by L. K. Frevel. The reciprocal lattice symmetry of C_{2h} and the extinction of $h0l$ for $h + l$ odd and $0k0$ for k odd established the space group $P2_1/n$, with measured unit cell parameters $a = 8.75$, $b = 9.79$, $c = 4.945$ A, and $\beta = 95.6°$. The calculated crystal density of 1.640 g cm^{-3} with $Z = 2$ agrees well with the experimental value of 1.627 measured by flotation. Multiple film Weissenberg methods were used to measure 610 Cu $K\alpha$ reflections. The 74 reflections for which $|E| \geq 1.5$ were used as input into the multiple solution computer program of Long,[9] which solved the phase problem through a reiterative application of Sayre's equation.[10] The correct solution, which assumed the signs of seven reflections, gave a consistency index of

$$C = \frac{\langle |E_h \Sigma_k E_k E_{h-k}| \rangle}{\langle |E_h| \Sigma_k E_{h-k} \rangle} = 0.97$$

after nine cycles. All seven heavy atoms were found unambiguously from an E map calculated with the 74 signs. The hydrogen atoms were subsequently located, and the structure was refined to a discrepancy index, $R_F = 0.13$, assuming anisotropic thermal parameters for C, N, and O.

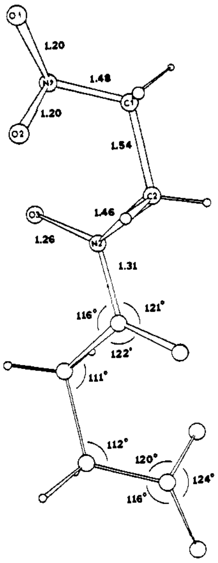

Figure 1. Bond distances and angles in 2-nitronitrosoethane dimer. The molecule is twisted into a conformation that brings the negatively charged nitro oxygen (O(2)) within 3.1 A of the nitroso nitrogen (N(2)) and serves to stabilize positive charge on N(2).

The molecular geometry with calculated bond distances and angles is shown in Figure 1. Two monomer units are bound in the *trans* configuration through the center of symmetry at the midpoint of the N–N bond. The six atoms C(2), N(2), O(3), C(2)′, N(2)′, and O(3)′ are nearly coplanar, and the bond angles at N(2) are approximately 120°. The bond lengths in the nitroso system are calculated to be N–N = 1.315 ± 0.010, N–C = 1.462 ± 0.008, and N–O = 1.255 ± 0.006 A. The latter two values differ significantly from the earlier results[7] for *p*-bromonitrosobenzene dimer (N–C = 1.40 and N–O = 1.35 A). The discrepancy cannot be reconciled by conjugation in the aromatic dimer since the bromophenyl groups are found to be twisted well out of the plane of the nitroso system. The calculated bond angles at the carbon atoms and in the nitro group are essentially normal,[11] as are the corresponding bond distances.

A molecular orbital calculation on 2-nitronitrosoethane has been performed using a nonempirical method[12,13] in which parameters for constructing the Hamiltonian matrix are derived from self-consistent-field (SCF) calculations on appropriate model compounds. In this method,[12] the overlap and kinetic energy integrals between all atomic orbitals in the system are evaluated exactly, while the SCF models yield values[14] for the diagonal Hamiltonian matrix elements (α's) and the coefficients K which are used in a modified Mulliken approximation to give the off-diagonal potential energy parts of the Hamiltonian. The results, expressed in terms of Mulliken net charges and overlap

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Table I. Molecular Orbital Results

A. Net Atomic Charges			
O(1)	−0.74	H(1) (av)	+0.03
O(2)	−0.69	H(2) (av)	+0.05
N(1)	+1.57	N(2)	+0.92
O(1)	−0.18	O(3)	−0.88
C(2)	−0.15		
B. Mulliken Overlap Populations[a]			
O(1)-N(1)	0.82	C(2)–H(2) (av)	0.62
O(2)–N(1)	0.84	C(2)–N(2)	0.72
N(1)–C(1)	0.75	N(2)–O(3)	0.71 (0.07)
C(1)–C(2)	0.81	N(2)–N(2)′	1.00 (0.24)
C(1)–H(1) (av)	0.69		

[a] π contribution to overlap population is indicated by parentheses.

populations,[15] are shown in Table I. Overlap populations should not be confused with bond orders: calculated overlap populations for a variety of molecules are available for purposes of comparison in ref 13. The nitro groups give a partial check on the degree of charge exaggeration in our wave function. The group dipole moment obtained from our calculated net charges is 4.5 D., compared to the experimental value in nitromethane of 3.5 D. Hence, we feel that while our net charges are moderately overestimated because of the lack of an explicit SCF procedure in the computations, the error thus introduced should not seriously modify our conclusions.

The molecular orbital results for the nitroso part of the system provide evidence that resonance structure II makes a very substantial contribution to the bonding in C-nitroso dimers. The overlap populations indicate that the π system perpendicular to the O–N–N–O plane contributes considerable double bond character to the N–N bond, but relatively little to N–O. This result is closely associated with the form of the highest filled molecular orbital (of symmetry u) which has nodes near the midpoints of the N–O bonds. Furthermore, the calculated charge distribution shows that the N–O bond is highly polar, even allowing for some charge exaggeration. The N–N bond length of 1.315 A is consistent with this interpretation, being considerably shorter than the value[16] of 1.41 A for the single bond in $N_2H_6^{2+}$, where adjacent nitrogen atoms may also be expected to bear large positive charges. The short distance and high stretching frequency of N–O with respect to single bond values are then attributed chiefly to coulombic attraction and only secondarily to the small amount of π character indicated in the overlap population. Contributions from other resonance structures, acting so as to reduce the polarization associated with the formal charges of II, are to be expected and are in fact implied by the population analysis.

Acknowledgment. We wish to thank L. K. Frevel for suggesting the problem and D. R. Petersen, J. H. Enemark, and J. J. Flynn for their generous assistance.

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F. Peter Boer
The Dow Chemical Company, Eastern Research Laboratory
Wayland, Massachusetts 01778

June W. Turley
The Dow Chemical Company
Chemical Physics Research Laboratory
Midland, Michigan 48640

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Perdeuteriostilbene. The Role of Phantom States in the *cis–trans* Photoisomerization of Stilbenes

Sir:

The following deals with the sensitized and direct *cis–trans* photoisomerization of perdeuteriostilbene. In interpreting the data, we have modified the triplet mechanism for sensitized isomerization and suggest a new mechanism for direct photoisomerization.

trans-Perdeuteriostilbene was synthesized from *cis*-perhydrostilbene by four exchanges with heavy water over platinum at about 200°.[1] Mass spectroscopic analysis showed that the *trans*-perdeuteriostilbene used is 80% d_{12}, 14% d_{11}, 4.3% d_{10}, and 1% d_9.[3] Irradiations were carried out in a merry-go-round apparatus.[4] Samples were degassed. A uranium glass filter (cutoff $\lambda \leq 3300$ A) was used for sensitized isomerizations and a 3130 A "filter train" for unsensitized isomerizations. Photostationary states were approached from *trans*-perdeuteriostilbene. Generally, *trans*-perdeuteriostilbene and *cis*- and *trans*-perhydrostilbenes were irradiated simultaneously. Analyses were by vapor phase chromatography.

Triplet-State Path. A phantom (twisted) triplet state, nearly isoenergetic and in equilibrium with the *trans* triplet, was suggested as a key intermediate in the sensitized photoisomerization of the stilbenes.[4] To account for small temperature effects on photostationary states it was assumed that phantom triplet decay to *cis* S^0 is more probable than *trans* triplet decay to *cis* S^0, and that the phantom triplet has higher enthalpy content than the *trans* triplet.[4] The estimate of the lifetime of stilbene triplets, 10^{-8} sec, depends on the assumption that excitation transfer from stilbene triplets to azulene (eq 1) is diffusion controlled.[4]

$$t\text{T}^1 + \text{Az}\text{S}^0 \xrightarrow{k_q} t\text{S}^0 + \text{Az}\text{T}^1 \tag{1}$$

We find that: (1) several sensitizers lead to photostationary compositions which are, within experimental uncertainty, identical for perdeuterated and undeuterated stilbene;[5] (2) for benzophenone-sensitized isomerization *trans* → *cis* quantum yields are identical for the two stilbenes.

Deuteration decreases the rate of $T^1 \rightarrow S^0$ radiationless decay.[6] Theory predicts the effect to diminish as the energy separation between electronic states decreases.[7] Deuteration, then, should affect *trans* triplet decay more than phantom triplet decay. The absence of a deuterium effect leads to the conclusion that *decay from trans triplets is negligible for both perhydro- and perdeuteriostilbene.* The supposed requirement that the phantom triplet be at higher energy than the *trans* triplet is removed.[8] Figure 1 shows a modified potential energy diagram for the triplet state ($k_1 \ll k_2$

(1) We find disproportionation to bibenzyl and phenanthrene to be a significant side reaction.[2]

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(8) A higher activation energy for decay of phantom triplets to *cis* ground state than to *trans* ground state could account for the temperature effect.