extinction coefficients, on the other hand, are found to increase at the higher temperature (Table I and Figure 5), which would be expected if the polarity of the medium is decreased.

In dioxane–water mixtures[14] (0–50 wt %), the dielectric constant is known to decrease by a constant fraction, *viz.* 9–10%, as the temperature is increased from 25 to 45°, the value of this fraction being almost independent of the composition of the solvent mixture. Assuming that similar decreases occur in ethylene glycol–water mixtures, values of D at 45° may be estimated to be 71.7, 59.9, and 33.9 for 0, 40, and 100 vol % ethylene glycol, respectively. The observed increases in ϵ_{290} at 45° are about those expected from Figure 4, for 0 and 40 vol % ethylene glycol; the increase for pure ethylene glycol is somewhat higher than the expected value. In view of the approximate nature of the calculations involved, the above agreements may be considered to be fair. Thus, the observed temperature effect can be explained largely in terms of the decrease in the polarity of the bulk medium at the higher temperature.

If it is assumed that the shape of the pyridinium bromide CT band, when log ϵ is plotted against λ, remains unchanged over the temperature range 25–45°, as has been observed for pyridinium iodide[9] bands, then the magnitudes of the red shifts for the same temperature range are 1.3–1.4 mμ for the three solvents. This is comparable to the 2-mμ shift in the red observed for the micellar CT band in dodecylpyridinium iodide.[11] The blue shifts in the pyridinium iodide CT bands, reported by earlier workers,[5,13] due to cooling may be at least partly because of an increase in the dielectric constant of the medium at the lower temperature.

Assuming that the pyridinium bromide band shape remains unaltered also over the dielectric constant range 78.5–37.7, the total red shift in going from water to ethylene glycol is only 8.5 mμ (Figure 5), considerably less than the 30-mμ red shift observed in the case of pyridinium iodide.[10] This indicates that the effect of solvent polarity is actually less on the position of the bromide band than on that of the iodide band.

The uv absorption behaviors at 25 and 45° for the long-chain compound, dodecylpyridinium bromide[15] (DPB), in 100% ethylene glycol are found to be very similar to those of EPB at these temperatures. The observed OD's are, however, slightly higher for DPB. This might be due to some premicellar association effects in DPB which presumably forms micelles[16] in pure ethylene glycol.

Acknowledgment. It gives the author great pleasure to thank Dr. G. Némethy for his interest in this work.

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Structure and Stability of the Nitric Oxide Dimer

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Abstract: Approximate nonempirical SCF–MO calculations using a minimum basis of Slater atomic orbitals have been made on the most likely structures of the nitric oxide dimer. The planar trans configuration has been found to have the lowest energy, with the following optimum geometry: R(NO) = 1.23, R(NN) = 1.53 Å, NNO = 104.6°. The optimum cis geometry has an energy 3.5 kcal/mol higher, and the near-rectangular structure suggested by X-ray evidence has an energy 66 kcal/mol higher. The dissociation energy of the dimer has been estimated by calculating the energy for the reaction $(NO)_2 + H_2 \rightarrow 2HNO$ and using an experimental energy for $HNO \rightarrow 0.5H_2 + NO$. The resulting value of 3.6 kcal/mol is near the upper limit of the experimental estimates.

In this paper we report the results of *ab initio* minimal-basis SCF calculations for the nitric oxide dimer and for the molecule HNO. Our aim is to calculate reliable bond lengths and angles of $(NO)_2$ at equilibrium in the gas phase, and assign a structure. Calculations on the closed-shell molecule HNO are carried out first to test the reliability of the method for a species containing the N–O bond, and second to estimate the energy of $(NO)_2$ by calculating the energy of

$$(NO)_2 + H_2 \longrightarrow 2HNO$$

and using an experimental energy for the reaction

$$HNO \longrightarrow 0.5H_2 + NO$$

The nitric oxide dimer has been postulated as an important intermediate in several gas-phase reactions of nitric oxide, most recently in a study of the chemiluminous NO + O reaction.[2] It was inferred some years ago from X-ray crystallography of the solid[3] and from the magnetic susceptibility[4a] and vibrational spectra[4] of the liquid and solid that nitric oxide in its condensed phases consists almost entirely of dimer molecules. Only recently, however, has the gas-phase dimer been observed directly, by mass spectroscopy[5] and in the infrared spectrum of NO gas.[6]

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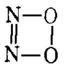
Dulmage, Meyers, and Lipscomb[3] concluded from the X-ray diffraction of solid NO that $(NO)_2$ was nearly rectangular, having short N=O bonds but a distance greater than 2 Å between the two NO moieties. The most recent analysis of their data[7] gives a trapezoidal structure with R(NO) = 1.12, R(NN) = 2.18, and R(OO) = 2.62 Å. Error estimates on the basis of isotropic temperature factors were approximately ±0.03 Å, but it is stated that these errors would be larger if the temperature factors were found to be anisotropic. From the X-ray data it was also not possible to distinguish definitely between head-to-head and head-to-tail arrangements of the two NO groups.

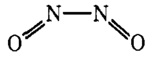
In the vibrational spectra of pure solid NO,[4] of matrix-isolated NO clusters,[4b,8] and of liquid and gaseous NO,[4a,6] two stretching frequencies are observed which have been assigned to the same form of $(NO)_2$. The higher of these, near 1860 cm^{-1}, appears in the Raman as well as the ir of the liquid[4a] and is taken to be the symmetric stretch; the lower, near 1770–1780 cm^{-1}, must therefore be assigned to the antisymmetric stretching mode. Since a centrosymmetric $(NO)_2$ should not have an infrared-active symmetric stretch, the most abundant form of $(NO)_2$ is apparently noncentrosymmetric.

Isotopic substitution experiments, which show the equivalence of the two nitrogen atoms and of the two oxygen atoms, rule out structures such as O=N—O=N.[8] The presence of an N–N bond in the dimer is further suggested by the formation of $(NO)_2$ in an argon matrix from N_2O and atomic oxygen.[8] Cyclic structures, such as

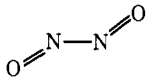


in which one would expect a short O–O bond, are eliminated by the fact that the observed stretching frequencies are characteristic of N–O double bonds rather than N–O single bonds.[4b,8] The frequency of nitric oxide itself is 1876 cm^{-1}.[6]

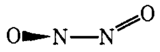
The structure of $(NO)_2$ is therefore generally taken to be cis (I), and in the solid the X-ray data suggest it is



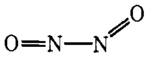
I



II



III



IV

nearly rectangular with a long N–N bond. The nonplanar skew forms (III), derived from the cis by internal rotation about the N–N bond, and forms in which the two NNO angles are unequal, of which the semilinear structure IV is one extreme, are not ruled out by any of the evidence from vibrational spectroscopy. There is also evidence for a trans form of $(NO)_2$,[4b,8] which has a single frequency near 1740 cm^{-1} assigned to an antisymmetric stretching mode. This frequency has been observed alongside of the stronger absorption bands attributed to the cis form, and its band shape has a different temperature dependence.

Method of Calculation

Ab initio all-electron calculations were performed using the Roothaan (LCAO) modification of the Hartree–Fock equations.[9] Molecular orbitals were expanded in terms of a minimal set of Slater-type atomic orbitals. The computer program was developed for an ICT 1905 computer by V. Saunders. It has the merit of being fast, and hence suitable for studies of potential energy surfaces, at the expense of some accuracy in the multicenter two-electron integrals. However, both total energies and relative energies from this program compare reasonably well with those from other published calculations.[10]

The results we shall present show energies minimized with respect to molecular dimensions and orbital exponents. In each case, optimization over n variables was accomplished by finding total energies at $^1/_2(n + 1)\cdot(n + 2)$ points scattered rather evenly about the suspected minimum. These points were then used to construct a quadratic fit, including cross terms, to the potential surface being investigated. This procedure worked well provided that one had an even distribution of points about the minimum. We believe our optimum points to be reliable, but a more serious question is to what extent the optimum geometries from a minimum-basis calculation can be expected to agree with experimental geometries. With this aim in mind, we quote first our results for HNO, for which an experimental geometry is well established. This we felt was preferable to an examination of NO itself, as it is difficult to compare the accuracy of SCF calculations for open- and closed-shell molecules.

For the 1s atomic orbitals of nitrogen and oxygen, we used the best free-atom exponents[11] (6.665 and 7.658, respectively), and for the valence orbitals we used the values given as optimal for HNO in its experimental geometry by Hehre, *et al.*;[12] $\zeta_{2s} = \zeta_{2p} = 1.95$ for nitrogen and $\zeta_{2s} = \zeta_{2p} = 2.25$ for oxygen.

The hydrogen exponent changes significantly with geometry and was therefore varied simultaneously with the HNO geometrical parameters (H–N length, HNO angle, and N–O length) in an overall optimization. The results are shown in Table I. The hydrogen exponent has decreased by nearly 9% from the value 1.31 given by Hehre and coworkers.[12] However, we found that further variation of the N and O valence-orbital exponents led to no significant change in the total energy. The agreement between the calculated and ex-

Table I. Calculated Geometry and Energy of HNO

	Calcd	Exptl[a]
R(NH), Å	1.116	1.063
R(N=O), Å	1.223	1.212
∠HNO, deg	105.1	108.6
ζ_H	1.211	
$-V/2T$	1.0011	
E, au	−129.3359	

[a] See L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

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Table II. Calculated Geometries and Energies of $(NO)_2$[a]

Structure	R(NN)	∠NNO	R(NO)	$-V/2T$	$-(E + 257.0)$	Energies, kcal/mol, relative to trans
Trapezoidal (X-ray)	(2.18)	(90)	(1.1)	1.0022	0.45550	66
Linear $(2\pi_g)^4$	(1.50)	(180)	(1.23)	1.0019	0.22083	214
Linear $(5\sigma_u)^2(2\pi_g)^2$	(1.50)	(180)	(1.23)	0.9983	0.30712	160
Semilinear (IV)	1.55	107.4 (180)	(1.23)	1.0016	0.40529	98
Cis (I)	1.57	110.2	1.23	1.0017	0.55571	3.5
Skew (III) 45°	(1.56)	(108.8)	(1.23)	1.0033	0.55791	2.1
Skew (III) 90°	(1.55)	(107.4)	(1.23)	1.0033	0.55748	2.4
Skew (III) 135°	(1.54)	(106.0)	(1.23)	1.0033	0.56104	0.2
Trans (II)	1.53	104.6	1.23	1.0016	0.56132	0

[a] Bond lengths in ångströms, angles in degrees, and energies in atomic units (1 au = 627.5 kcal/mol). Values in parentheses have not been optimized to an energy minimum.

perimental[13] NO bond lengths is very encouraging. The deviations of the NH bond length and HNO angle from the experimental values are comparable with those found by Pitzer and Merriifield[14] in minimal-basis calculations on H_2O.

Calculations on $(NO)_2$

Using the same basis as for HNO, we performed calculations for the various structures of $(NO)_2$ summarized in Table II.

Several calculations were done for linear $(NO)_2$. Convergence to an open-shell $2\pi_g^2$ configuration was obtained from our SCF program in its normal form. Our calculated energy is for a pseudo-closed-shell configuration $(2\pi x_g^2)$, which is a mixed $^1\Sigma_g$ and $^1\Delta_g$ state. Extended Hückel calculations[15] have suggested that the linear NO dimer should have a closed-shell $2\pi_g^4$ configuration (obtained by promoting two electrons from $5\sigma_u$). By choosing a starting density matrix appropriate to this, we were able to iterate to an SCF wave function, but its energy was much higher than for the open-shell configuration. As both energies were much higher than for the cis or trans configurations, we did not study them in more detail.

The near-rectangular structure deduced from the X-ray analysis has a considerably higher energy than the optimum cis or trans structures, and this can be directly attributed to the absence of a short N-N bond. We find very little difference between the optimum bond lengths and angles for the cis and trans configurations. The N-N bond length and ONN bond angle are both slightly larger for the cis molecule, which suggests that the type of calculation we have made is able to represent features of geometry which would normally be attributed to steric factors.

We calculate an N-N bond length for the cis and trans configurations which is considerably shorter than that of N_2O_4 but slightly longer than that in hydrazine (N_2H_4). The molecule cannot be adequately represented by two weakly interacting NO fragments.

Energies have been calculated for the skew geometry at three twist angles. The bond lengths and NNO angle were extrapolated from the cis and trans configurations by assuming them to be linear functions of the twist angle. No further optimization of these parameters was attempted. We find a subsidiary energy maximum at a 90° twist, but in view of the incomplete geometry optimization we place no significance on this.

Our calculations show that the cis configuration has the maximum energy for variation in the twisting coordinate. The situation is therefore different from that encountered for butadiene (with which it is isoelectronic) for which the skew (90°) configuration has an energy maximum.[16]

If we examine the Mulliken overlap populations[17] for the N-N bond in the cis, trans, and skew (90°) configurations, which are defined by

$$\rho_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} P_{\mu\nu}S_{\mu\nu}$$

where $P_{\mu\nu}$ and $S_{\mu\nu}$ are respectively the density-matrix element and the overlap integral for orbitals μ and ν on atoms A and B, respectively, we find

	P_{NN}^{σ}	P_{NN}^{π}	P_{NN}^{tot}
Cis	0.304	0.017	0.321
Skew (90°)			0.348
Trans	0.336	0.021	0.357

The separate σ and π contributions have been quoted for the cis and trans configurations. The results parallel those of the total energy, the total NN population increasing monotonically from cis to trans. We attribute the difference between $(NO)_2$ and butadiene to the fact that in $(NO)_2$ the nitrogen lone-pair orbitals can contribute to N-N bonding in the skew configuration, whereas the corresponding C-H bond electrons in butadiene cannot take part in C-C bonding without seriously weakening the C-H bond.

Our calculations predict that the molecule would be largely in the trans configuration in the gas phase. However, the energy required to twist to a skew configuration is very little and only 3.5 kcal/mol is required to give the cis configuration. The vibrational spectrum of gas-phase NO shows a dimer band at 1788 cm^{-1} which has P, Q, and R branches but no resolved rotational structure. A second band has been suggested to underlay the monomer absorption at 1880 cm^{-1} on the grounds of an irregular temperature dependence of the absorption in this region. If two strong ir bands are observed, then this would indicate a cis or skew configuration, contrary to our calculations. We do not feel that the evidence of the second band at 1860 cm^{-1} is strong enough for us to conclude that our calculations are unreliable.

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However, our finding that the trans molecule has the lowest energy may be an artifact of our minimum-basis calculation. There is some evidence from calculations on H_2O_2 that an extended basis, which includes d orbitals on the central atoms, is needed to give the correct stability to a skew configuration.[18] We therefore admit the possibility that in the gas phase the skew configuration is the stable form, but do not believe that the cis configuration is the most stable.

Dinerman and Ewing[6] have estimated a geometry for the gas-phase dimer from the contours of the 1788- and 1860-cm^{-1} absorption bands. The 1788-cm^{-1} band appears as a parallel band of a near-symmetric top, and the separation of the P and R branches determines the smallest moment of inertia I_c. The presence of the 1860-cm^{-1} band, which underlies the monomer peak, is shown by a temperature-dependent absorption in this region. It is found to be a perpendicular band of Gaussian shape, and from its half-width an asymmetry parameter $\beta = (I_c/I_a - 1)$ is determined. By assuming $R(NO) = 1.15$ Å, the monomer bond length, they obtain the best fit to their data with $R(NN) = 1.75$ Å and $\angle NNO = 90°$. An angle of 120° gives a slightly poorer fit of the data.

Although there must be large error limits in this analysis, the results do appear to be incompatible with the long N–N bond (2.18 Å) deduced from the X-ray data. Lipscomb[19] has suggested that further spectroscopic and other studies are needed to resolve this discrepancy. Our calculations support the short N–N bond length, but our calculated moments of inertia are not close to those found by Dinerman and Ewing. For comparison, we give those of our cis and trans configurations below (amu Å^2).

	I_a	I_b	I_c
Dinerman and Ewing	20	46	66
Cis	20	64	74
Trans	8	86	94

The trans configuration is seen to be closest to a symmetric-top molecule.

Although one can question the reliability of geometries deduced from minimum-basis SCF calculations, it is very unlikely that an extended basis or a calculation with configuration interaction would lead to the X-ray geometry, which in our calculation has an energy greater by 66 kcal/mol. Lipscomb[19] has pointed out that there are no abnormally short distances between different dimers in the solid, which would suggest that crystal forces are responsible for the gas and solid dimers having markedly different structures. We therefore believe that our calculations suggest that further X-ray studies would be profitable in an attempt to resolve the difficulty.

The Dissociation Energy of $(NO)_2$

Estimates of the enthalpy of dimerization of nitric oxide have been made from the temperature dependence of the intensities of the infrared absorptions of $(NO)_2$,[6] the temperature dependence of the second virial coefficient,[20,21] and from other thermodynamic data.[20] These estimates fall in the range 1.4–2.9 kcal/mol. SCF molecular orbital theory is not suitable for a direct calculation of the dimerization energy, because the correlation energy of 2NO and $(NO)_2$ may be very different. We have instead chosen to calculate the energy of the reaction

$$2HNO \longrightarrow H_2 + (NO)_2 \qquad \Delta E_1$$

and to use experimental data for the reaction

$$2HNO \longrightarrow 2NO + H_2 \qquad \Delta E_2$$

By subtraction, we have the dissociation energy of $(NO)_2$ equal to $\Delta E_2 - \Delta E_1$.

The experimental H–N bond energy of HNO is 48.6 kcal/mol[22] and the bond energy of H_2 is 104.2 kcal/mol.[23] After correcting for zero-point energy, ΔE_2 becomes −7.1 kcal/mol. Our calculated ΔE_1, using for H_2 the appropriate optimum 1s exponent,[10] is −11.1 kcal/mol. Thus the calculated dissociation energy of $(NO)_2$ is 4.0 kcal/mol. If we make a small allowance for the zero-point energy of the N–N stretching frequency, say 0.7 kcal/mol,[24] and correct ΔE_1 and ΔE_2 for thermal energy changes ($^1/_2RT$), we obtain a value of 3.6 kcal/mol, which is reasonably close to the upper limit of the experimental estimate for the dissociation energy.

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[24] Assuming that the 262-cm^{-1} fundamental in the Raman of the liquid (ref 3) arises from the NN stretch, by analogy with N_2O_3 [$\nu_{NN} = 253$ cm^{-1}: J. P. Devlin and I. C. Hisatsune, *Spectrochim. Acta*, **17**, 218 (1961)] and N_2O_4 [$\nu_{NN} = 265$ cm^{-1}: I. C. Hisatsune, J. P. Devlin, and S. Califano *ibid.*, **16**, 450 (1960)].