A Reinvestigation of the Structure and Torsional Potential of N_2O_5 by Gas-Phase Electron Diffraction Augmented by *Ab Initio* Theoretical Calculations

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Dedicated to Professor *Edgar Heilbronner* on the occasion of his 80th birthday. *K. H.* recalls with great pleasure both the stimulating scientific collaboration and the many enjoyable social occasions that took place over 50 years ago.

Gaseous N_2O_5 consists of two NO_2 groups bonded to a bridging O-atom to form a nonlinear N−O−N moiety. The NO_2 groups undergo slightly hindered internal rotation around the bonds to the bridge so that instantaneous composition of the gaseous system is characterized by molecules with all combinations of torsion angles. In an earlier investigation, an attempt was made to determine the coefficients for an empirical form of the double-rotor torsional potential, and the bond lengths and bond angles measured subject to assumptions that the structure of the $O-NO_2$ groups was invariant to torsion angle and that these groups had C_{2v} symmetry. The system has now been reinvestigated in terms of a more realistic model in which this symmetry restriction was relaxed, account was taken of structural changes in the NO_2 groups with torsion angle as predicted by *ab initio* theory at the B3LYP/6-311 + G* level, and a more convenient form of the torsional potential was assumed. The most stable conformation has C_2 symmetry with torsion angles τ_1 (defined as $\sphericalangle(N-O-N=O_4)$) equal to τ_2 (defined as $\sphericalangle(N-O-N=O_6)$) equal to 33.7°; because of the broad potential minimum in this region, the uncertainty in these angles is difficult to estimate, but is probably 3–4°. The results for the bond lengths and bond angles for the most stable conformation are $r_g(N-O) = 1.505(4)$ Å, $r_g(N=O) = 1.188(2)$ Å, $\sphericalangle_\alpha(N-O-N) = 112.3(17)°$, $\sphericalangle_\alpha(O=N=O) = 134.2(4)°$, $\langle \sphericalangle_\alpha(O-N=O) \rangle = 112.8(2)°$. The difference between the symmetry-nonequivalent O−N=O angles is estimated to be *ca.* 6.7° with the larger angle positioning the two N=O bonds on different NO_2 groups nearest each other. These *average* values are similar to those obtained in the original study. The main difference is found in the shape of the torsional potential, which at $\tau_1/\tau_2 = 0/0$ has a saddle point in the present work and a substantial peak in the earlier. The implication of the torsion-angle findings for electron-diffraction investigations of this type is discussed.

Introduction. – In a previous report [1], we described the results of a gas-phase electron-diffraction (GED) study of molecular N_2O_5. This work confirmed that the molecule consisted of two NO_2 groups linked by a bridging O-atom ($O_2N-O-NO_2$), and that the N−O−N moiety was nonlinear (*Fig. 1*). It also confirmed that the NO_2 groups were undergoing large amplitude motion, perhaps more accurately described as restricted internal rotation, about the bonds connecting them to the apical O-atom. The problem thus divided itself into two parts: the short-range structure of the molecule determined by the bond lengths and bond angles, and the long-range structure determined by the torsion angles of the two rotating groups, themselves dependent on the nature of the potential surface $V(\tau_1,\tau_2)$. The analysis of the short-range structure was straightforward and led to a size and shape of the NO_2 group similar to that previously measured in N_2O_4 [2] and to normal values for the bonds to, and the angle at, the apical O-atom. The long-range structure was more difficult since the distances between the NO_2 groups are washed out by the large-amplitude torsional motion. Such motion requires special methods to represent the scattering from the affected distances, which undergo large changes in magnitude. We followed our usual procedure [3] for representing the distribution of these distances by introducing a set of weighted 'pseudoconformers', *i.e.*, molecules characterized by fixed values of the torsion angles, which spanned the space defined by all values of the two torsion angles. In order that such a set of pseudoconformers satisfactorily represents a given system, it is necessary that both the number of conformers and their weights be chosen carefully. For N_2O_5, we spaced the conformers at torsion-angle intervals of 22.5° and gave each a *Boltzmann* weight, $P(\tau_1,\tau_2) = Q^{-1}\exp(-V(\tau_1,\tau_2)/RT$. Lacking information about the potential, it was assumed to have the form

$$V(\tau_1,\tau_2) = \tfrac{1}{2}V_0(2 - \cos 2\tau_1 - \cos 2\tau_2) + U_0\Sigma_i\Sigma_j(r_0/r_{ij})^{n}, \qquad (1)$$

which was designed to portray energy effects from the rotors independent of each other (cosine terms), modified by repulsions between the two NO_2 groups (*Lennard-Jones* terms). A good fit to the GED data was obtained with $V_0 = 1.90$ ($2\sigma = 0.24$) kcal/mol, and U_0, r_0, and n and assumed to be 0.1 kcal/mol, 2.8 Å, and 12, respectively. The minimum-energy conformation of the molecule was found to have C_2 symmetry with the two NO_2 groups rotated about 30° from the N–O–N plane ($\tau_1/\tau_2 = 30°/30°$; hereafter degree symbols are omitted in this ratio). *Fig. 2* shows the potential surface among which the important features are a peak of *ca.* 5 kcal/mol at $\tau_1/\tau_2 = 0/0$, corresponding to a planar molecule, and saddle points at $\tau_1/\tau_2 = -45/45$ and $45/-45$, all of which have eclipsed N=O bonds from different NO_2 groups. The form of this potential suggested that N_2O_5 moves from the $\tau_1/\tau_2 = 30/30$ conformation to the equivalent $\tau_1/\tau_2 = -30/-30$ by two paths, a lower-energy one that included a saddle point at $\tau_1/\tau_2 = 0/90$ (or 90/0) and another, higher energy path that included one at $\tau_1/\tau_2 = -45/45$ (or $45/-45$). Each saddle point had C_s symmetry.

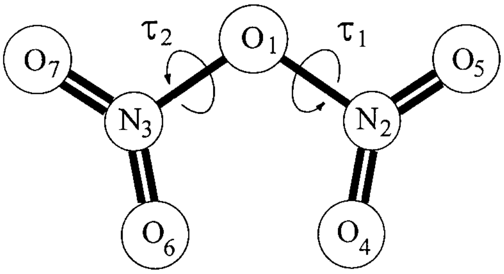

Fig. 1. *Diagram of the N_2O_5 molecule*

Subsequent to our previous report, several studies of the structure of N_2O_5 have been published. On the experimental side, the methods were infrared (IR) spectroscopy [4–6] and microwave (MW) spectroscopy [6–8], and, on the theoretical side, molecular orbital calculations at the *Hartree-Fock* [5][7][9][10]; density functional [7][5][11][12], and *Møller-Plesset* [5][7][10][11] levels of theory. The results from all of but one of these studies (the study by *Colmont* [8] led to no conclusions about the structure of the molecule) were gratifyingly consistent with our GED ones; among these was the discovery by *DeLucia et al.* [4] of a previously unobserved vibrational IR band near the frequency predicted from our GED work. There are, however, differences in some of the structural details obtained from the GED work and from the MW work of *Grabow et al.* [7]. For example, the MW study indicated that the N–O–N bond angle should be *ca.* 120.5° (GED value: 111.8(16)°), and the torsional angles in the C_2 minimum-energy structure *ca.* 41° (GED value: *ca.* 30°). There are also differences in some features of the torsional potential, most strikingly at $\tau_1/\tau_2 = 0/0$ where our work had a peak and that of *Grabow et al.* has a saddle point. Also, the barrier to interconversion of the two equivalent C_2 conformers from the MW work is suggested to be *ca.* 0.02 kcal/mol whereas the GED value of is *ca.* 0.5 kcal/mol. Although *Grabow et al.* did not provide full details of the potential surface, they deduced rough values for the coefficients of some of the potential-function terms based on their MW results. The surface corresponding to these rough values is seen in *Fig. 3*; it is quite different from those obtained from the earlier GED work depicted in *Fig. 2.*

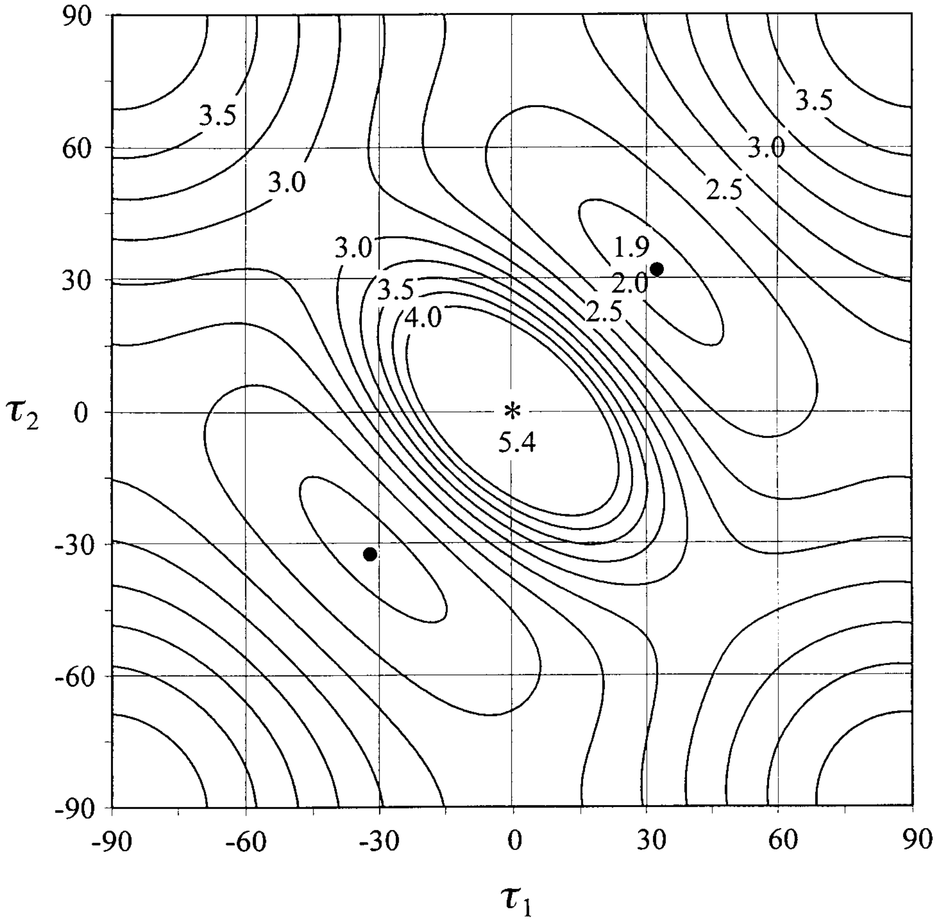

Fig. 2. *Potential surface obtained in previous electron-diffraction analysis of the N_2O_5 system with use of* Eqn. 1. Potential minima are indicated by black dots, and the highest point is shown by the asterisk at $\tau_1 = \tau_2 = 0°$.

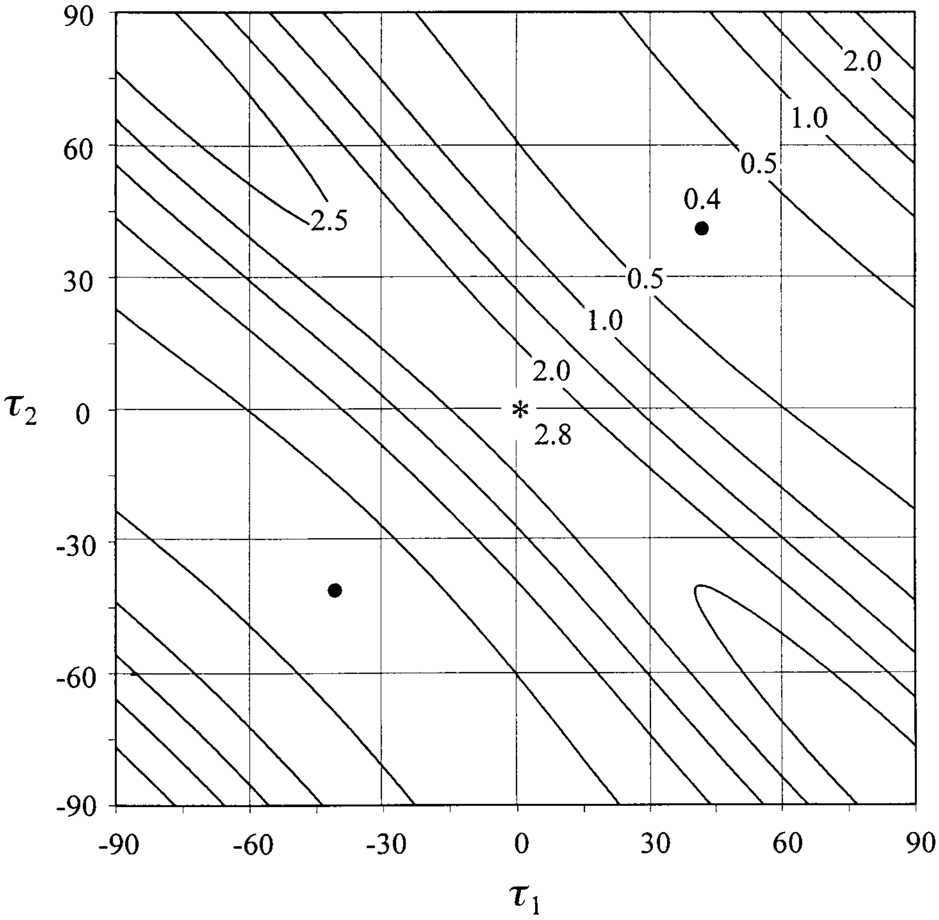

Fig. 3. *Potential surface obtained with use of potential constants from* [7]. Potential minima are indicated by black dots, and the asterisk at $\tau_1 = \tau_2 = 0°$ indicates a saddle point.

While it might be hoped that the theoretical studies could help to resolve these differences, this is not the case. Depending on the type and level of theory, the reported *ab initio* calculations have produced a range of apical N–O–N angles (108.3° [9] to 117.4° [11]) and torsion angles for the minimum-energy structure of C_2 symmetry of 21.0° [12] to 43.2° [5]. While none of these studies included an investigation of the entire potential-energy surface of N_2O_5, energies for the C_2 and $\tau_1/\tau_2 = 0/90$ conformers were usually calculated, and, again depending on the type and level of theory, the relative energies for these varied. In some calculations [5][11], the 0/90 conformer was predicted to have an even lower energy than the C_2 conformer.

With questions remaining about some aspects of the structure of N_2O_5, we decided to see what further information might be extracted from our GED data by use of results from theoretical calculations not available in our original study. The main objectives were to seek improved accuracy in the values of the structural parameters, and, possibly, in the parameters determining the torsional dynamics of the molecule, by using as constraints the results of reasonably high-level *ab initio* calculations in the analysis of the GED data. In the original work, for example, the structures of the $O-NO_2$ groups were assumed to have C_{2v} symmetry with distances and angles invariant with torsion angle. Although the *ab initio* values for bond distances and bond angles are not individually reliable to the accuracy provided by experiment, they do contain reliable predictions of the corresponding *changes* in the values of these parameters as they vary with torsion angle. Imposition of these changes, or differences, as constraints should improve the accuracy of the values. A second matter of interest was the torsion-dependent aspect of the structure. Although the double-rotor potential (*Eqn. 1*) assumed to describe the torsional potential is intuitively reasonable and provided a good fit to the GED data, it is entirely empirical and does not agree well with the theoretical results. For reasons to be discussed later, electron diffraction cannot be expected to yield reliable results for the torsional potential in systems such as N_2O_5. Nevertheless, a study of the quality of the fit between experiment and theory following from use of a more convenient type of potential seemed a worthwhile endeavor. We report here the results of our reinvestigation of N_2O_5.

Theoretical Calculations. – The purposes of the theoretical calculations were two: to provide a plausible picture of the entire potential surface, and to provide values of the structural parameters to be used for evaluation of differences among the pseudoconformers comprising the model for experimental testing. The theoretical potential surface offered a model for comparison with ones developed from experiment, and the theoretical parameter values would serve to establish the connections between the structures of the pseudoconformers with a reference form that would incorporate the parameters to be refined. We carried out *ab initio* molecular-orbital calculations with the program Gaussian98W [13] at the HF and B3LYP levels of theory with several basis sets, the largest being 6-311 + G(d). The results that form the basis of the work to be described are all from the B3LYP/6-311 + G(d) calculations and reflect optimizations at fixed torsion angles $-90 \leq \tau_1/\text{deg} \leq 90$ and $-90 \leq \tau_2/\text{deg} \leq 0$ at 15 degree intervals – a total of 91 pseudoconformers. They are listed in *Table 1*. Given the symmetry of the system, the results map the torsional potential over the entire range of both angles.

Structure Determination. – *Formulation of the Model.* The determination of the structure of a gas-phase molecule by electron diffraction is based on a satisfactory fitting of a theoretical electron-scattering intensity distribution for a model of the molecule (or system of molecules) to the experimental intensity distribution. The fitting is done by a least-squares adjustment of parameters that specify all aspects of the molecule or system – in the case of N_2O_5, bond distances, bond angles, root-mean-square amplitudes of vibration, and the nature of the large-amplitude torsional motion. As in our earlier work, the analysis of the torsional motion was based on an assembly of pseudoconformers intended to provide an adequate representation of the continuous distribution of torsion-sensitive distances over the entire range of both torsion angles. As described in the *Introduction*, this representation is obtained by giving each conformer a *Boltzmann* weight determined by the torsional potential $V(\tau_1,\tau_2)$. The

Table 1. *N_2O_5: Theoretical Energies* [a]) ($E_h + 485.0$) *for Structures Optimized for Various Combinations of Two Torsion Angles* [deg]

τ_1	$\tau_2 = 90$	75	60	45	30	15	0
90	– 0.4695402	– 0.4704270	– 0.4725440	– 0.4753212	– 0.4780636	– 0.4800124	– 0.4806908
75	– 0.4704270	– 0.4716129	– 0.4738723	– 0.4766505	– 0.4791553	– 0.4805938	– 0.4806213
60	– 0.4725440	– 0.4738723	– 0.4760217	– 0.4784618	– 0.4803295	– 0.4810181	– 0.4804551
45	– 0.4753212	– 0.4766505	– 0.4784618	– 0.4801913	– 0.4811952	– 0.4811527	– 0.4801978
30	– 0.4780636	– 0.4791553	– 0.4803295	– 0.4811952	– 0.4813967	– 0.4808634	– 0.4798185
15	– 0.4800124	– 0.4805938	– 0.4810181	– 0.4811527	– 0.4808634	– 0.4801987	– 0.4794236
0	– 0.4806908	– 0.4806213	– 0.4804551	– 0.4801978	– 0.4798185	– 0.4794236	– 0.4792464
– 15	– 0.4800124	– 0.4793333	– 0.4789267	– 0.4786980	– 0.4786325	– 0.4788506	– 0.4794236
– 30	– 0.4780636	– 0.4771631	– 0.4768961	– 0.4770759	– 0.4776558	– 0.4786325	– 0.4798185
– 45	– 0.4753212	– 0.4746230	– 0.4748292	– 0.4757057	– 0.4770759	– 0.4786980	– 0.4801978
– 60	– 0.4725440	– 0.4722961	– 0.4731808	– 0.4748292	– 0.4768961	– 0.4789267	– 0.4804551
– 75	– 0.4704270	– 0.4707105	– 0.4722961	– 0.4746230	– 0.4771631	– 0.4793333	– 0.4806213
– 90	– 0.4695402	– 0.4704270	– 0.4725440	– 0.4753212	– 0.4780636	– 0.4800124	– 0.4806908

[a]) B3LYP/6-311 + G(d). Some of the entries are identical because of symmetry.

bond distances and bond angles of these individual pseudoconformers will be slightly different and cannot, of course, be measured. However, if these parameter values are tied to those of just one of the conformers, the parameters of that reference conformer describe the structures of all the others subject to the assumptions connecting them.

The problem of the large amplitude motion is essentially one of determining the appropriate weighting for each of the pseudoconformers. This is done indirectly, *i.e.*, by assuming a form for the potential and varying its parameters to obtain the best fit. If the theoretical potential were correct, the final conformational weighting in the N_2O_5 system would be determined solely from the theoretical energies of the pseudoconformers. If, as is probable, the weighting from theory is not consistent with experiment, adjustments are required. One scheme for such adjustments would be to model the potential surface with a polynomial having adjustable coefficients. This approach is unappealing, however, because there would be no obvious connection between the result and the structure of the molecule. Such a connection is provided by the form of our original empirical potential, but this potential would be more awkward to implement in the present study than in the earlier one, because the assumption that the bond distances and bond angles were the same for all pseudoconformers was now to be dropped. For these reasons, a better form for the potential is that proposed by *Grabow et al.* [7]:

$$\begin{aligned} V(\tau_1,\tau_2) = & -V_{\mathrm{gear}} \cos\,[2(\tau_2 - \tau_1)] + V_{\mathrm{antigear}} \exp\,(\delta\,[1 - \sin^2\,(\tau_2 - \tau_1)]) \\ & + V_{\mathrm{linear}}\,(\cos 2\tau_1 + \cos 2\,\tau_2), \end{aligned} \tag{2}$$

which has only torsion angles as variables, and which was shown by tests to be capable of approximately duplicating the theoretical potential. This first term of this function represents gear-like motion of the two NO_2 groups, the second term weights against antigear motion of these groups; and the last term permits a minimum at a point other than $\tau_1/\tau_2 = 45/45$.

Our model of the N_2O_5 system was designed following the ideas outlined above. It included the 43 unique pseudoconformers covering the ranges $0 \leq \tau_1/\mathrm{deg} \leq 90$ and $-75 \leq \tau_2/\mathrm{deg} \leq 90$ at 15° intervals to represent the large-amplitude motion¹). The pseudoconformer with $\tau_1 = \tau_2 = 30°$ (C_2 symmetry) seemed likely to be close to the potential minimum and was chosen as the reference conformation; the bond lengths and bond angles of the other conformers were tied to it, imposing the calculated theoretical differences. The interatomic distances for each conformer resulting from inclusion of these differences were of a type symbolized by r_α and required corrections for the effects of vibrational averaging. We used the previously calculated [1] corrections, interpolating as necessary. The *Boltzmann* weight of each conformation was derived from the torsional potential defined by *Eqn. 2*. The adjustable structural parameters (in r_α space and applying to the reference conformation) were $r(\mathrm{N{-}O})$, the averages $\langle r(\mathrm{N{=}O})\rangle = 1/2[r(\mathrm{N_2{=}O_4}) + r(\mathrm{N_2{=}O_5})]$ and $\langle \measuredangle(\mathrm{O{-}N{=}O})\rangle = 1/2[\measuredangle(\mathrm{O_1{-}N{=}O_4}) + \measuredangle(\mathrm{O_1{-}N{=}O_5})]$, and the differences $\Delta r(\mathrm{N{=}O}) = r(\mathrm{N_2{=}O_5}) - r(\mathrm{N_2{=}O_4})$, $\Delta\measuredangle(\mathrm{O{-}N{=}O}) = \measuredangle(\mathrm{O_1{-}N{=}O_4})$, and $\Delta\measuredangle(\mathrm{N{-}O{-}N{=}O_5}) = \measuredangle(\mathrm{N{-}O{-}N{=}O_5}) - (\tau_1 - 180°)$; the last takes into account possible nonplanarity of the ONO_2 groups. The adjustable potential-function parameters were V_{gear}, V_{antigear}, V_{linear}, and δ. Each pseudoconformer was assumed to undergo molecular vibrations of its frame similar to those of any molecule. The amplitude parameters describing the result of these vibrations were chosen as $l(\mathrm{N{-}O})$, $l(\mathrm{N{=}O})$, $l(\mathrm{N \cdots N})$, and $l(\mathrm{N_2 \cdots O_6})$, which represent groups of amplitudes that include contributions from all pseudoconformers; the amplitude values for the members of these groups were tied to those of the reference pseudoconformer by the theoretical differences. Finally, we took account of the possible presence of NO_2 and O_2 as impurities by including them in adjustable amounts. The model consisting of the 43 pseudoconformers and the two hypothetical impurities had a total of 906 interatomic distances and was specified by four distance, three bond-angle, and one torsion-angle parameter, four vibrational-amplitude parameters, and four potential-function parameters.

Electron-Diffraction Data. The data described in our previous study was used. Near the end of the refinement, new backgrounds (which are subtracted from the total scattered intensity to produce the scattering sensitive to the molecular structure) were calculated, resulting in a slightly different set of average intensity curves. These curves are shown in *Fig. 4*.

Refinement Results. The refinements were carried out by a least-squares fitting of theoretical intensities to the average experimental intensities [14]. The parameters were those described above. Because of high correlations with other parameters, the three difference parameters were held fixed at values obtained from the *ab initio* calculations during all refinements. The vibrational anharmonicity corrections used in the previous study were applied. For one refinement, resulting in our final model A, three of the four potential-energy-function parameters of *Eqn. 1* (V_{gear}, V_{antigear}, and V_{linear}) were refined; the fourth parameter δ was held at the value suggested by *Grabow et al.* In a second refinement, resulting in final model B, all four potential function

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¹) Although the specified angle ranges include data for 91 conformations, only 43 are unique because of symmetry.

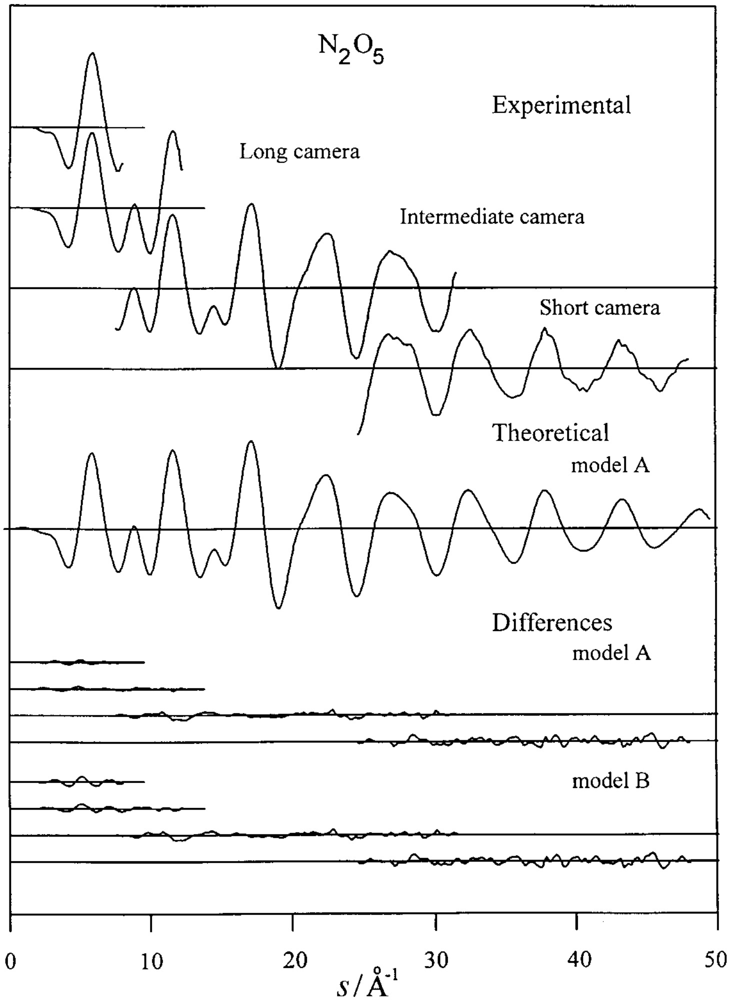

Fig. 4. *Scattered intensity distribution from electron diffraction of N_2O_5.* Intensity scale is arbitrary. The abscissa scale is $s = 4\pi\lambda^{-1}\sin\theta$ where θ is half the scattering angle. The experimental curves were obtained from three different distances between nozzle tip and photographic plate. The difference curves are experimental minus theoretical.

parameters were held fixed at the values suggested by *Grabow et al.* The results of these refinements are summarized in *Table 2* in terms both of the reference conformation ($\tau_1 = \tau_2 = 30°$) and the conformation of greatest stability as deduced from the electron-diffraction data by methods to be described later. Distances and amplitudes for both of these conformations are found in *Table 3* for our preferred model A, and the correlation matrix for the refined parameters of this model is given in *Table 4.* Intensity curves are shown in *Fig. 4*, radial distribution curves in *Fig. 5*, and the torsional potential in *Fig. 6.*

Table 2. *N_2O_5: Structural Results for Most Stable Conformation and Reference Conformation*

Most stable conformation		Reference conformation				
Parameter^{a})	Model A	Model A	Model B	Parameter^{a})	Model A	Model B
r_α(N–O)	1.499(4)	1.499(4)	1.497(4)	V_{gear}^{b})	– 0.96(525)	[0.0]
$\langle r_\alpha$(N=O)$\rangle$^{c})	1.185(2)	1.183(2)	1.183(1)	$V_{antigear}$^{b})	4.9(242)	[0.343]
Δr_α(N=O)^{d})	[– 0.002]	[– 0.001]	[– 0.001]	V_{linear}^{b})	– 5.0(247)	[– 0.114]
$\sphericalangle_\alpha$(O=N=O)	134.2(4)	134.3(4)	134.1(4)	δ^{b})	[2.0]	[2.0]
$\sphericalangle_\alpha$(N–O–N)	112.3(17)	113.3(15)	113.6(17)	% impurity^{e})	8.8(40)	9.3(43)
$\langle \sphericalangle_\alpha$($O_1$–N=O)$\rangle$^{f})	112.8	112.8(2)	112.8(2)	R^{g})	0.066	0.071
$\Delta \sphericalangle_\alpha$($O_1$–N=O)^{h})	[– 6.0]	[– 6.7]	[– 6.7]			
$\Delta \sphericalangle_\alpha$(N–O–N=$O_4$)^{i})	[0.1]	[3.14]	[3.14]			
$\tau_1 = \tau_2$^{j})	33.7	[30.0]	[30.0]			
oop^{k})	5.0	4.7	4.7			

^{a}) Distances (r_α) are in Å, potential constants (V) in kcal/mol. Quantities in parentheses are estimated 2σ, those in square brackets were assumed. ^{b}) Potential function parameters from *Eqn 1*. ^{c}) Equal to $1/2[r_\alpha(N{=}O_4) + r_\alpha(N{=}O_5)]$. ^{d}) Equal to $r_\alpha(N{=}O_5) - r_\alpha(N{=}O_4)$. ^{e}) Impurity taken as $2NO_2 + 1/2O_2$. ^{f}) Equal to $1/2[\sphericalangle(O_1{-}N{=}O_4) + \sphericalangle(O_1{-}N{=}O_5)]$. ^{g}) Goodness-of-fit factor, equal to $\Sigma_i w_i \Delta_i^2 / \Sigma w_{il} \{s_i[I_i(\text{obs.})]\}^2$ where $\Delta_i = s_i I_i(\text{obs.}) - s_i I_i(\text{calc.})$. ^{h}) Equal to $\sphericalangle(O_1{-}N{=}O_5 - <(O_1 - N{=}O_4)$. ^{i}) Defined as $\sphericalangle(N{-}O{-}N{=}O_5) - (\tau_1 - 180°)$ where $\tau_1 = 30°$ for the reference conformer. ^{j}) Torsion angle: $\tau_1 = \sphericalangle(N_3{-}O_1{-}N{=}O_4)$, $\tau_2 = \sphericalangle(N_2{-}O_1{-}N{=}O_6)$. ^{k}) Out-of-plane angle: angle between plane of NO_2 group and projection of O–N bond.

Table 3. *N_2O_5: Interatomic Distances and Vibrational Amplitudes for Most Stable Conformation and Reference Conformation*^{a})

Most stable conformation ($\tau_1 = \tau_2 = 33.7°$ ^{b})						Reference conformation ($\tau_1 = \tau_2 = 30°$ ^{b})				
term	r_α ^{c})	r_g ^{d})	r_a ^{e})	l		r_α ^{c})	r_g ^{d})	r_a ^{e})	l	
N–O	1.499(4)	1.505	1.503	0.055(5)		1.499(4)	1.505	1.503	0.055(5)	
N=O_4	1.184	1.189	1.188	0.036	(2)	1.184(1)	1.189	1.188	0.036	(2)
N=O_5	1.183	1.187	1.187	0.036		1.183(1)	1.188	1.187	0.036	
$O_1 \cdot O_4$	2.279	2.286	2.284	0.060	(5)	2.283(5)	2.290	2.288	0.060	(5)
$O_1 \cdot O_5$	2.202	2.208	2.206	0.059		2.197(5)	2.203	2.202	0.059	
$O_4 \cdot O_5$	2.181	2.186	2.185	0.041		2.181(4)	2.186	2.185	0.041	
$N \cdot N$	2.489	2.500	2.493	0.119		2.505(24)	2.515	2.509	0.119	
$N_3 \cdot O_4$	2.70	2.72	2.706	0.15	(2)	2.71(4)	2.72	2.71	0.15	(2)
$N_3 \cdot O_5$	3.45	3.46	3.455	0.07		3.47(2)	3.48	3.48	0.07	
$O_4 \cdot O_6$	2.65	2.67	2.650	0.22		2.59(5)	2.61	2.59	0.22	
$O_4 \cdot O_7$	3.66	3.67	3.664	0.15		3.71(3)	3.72	3.72	0.15	
$O_5 \cdot O_7$	4.37	4.27	4.370	0.05		4.37(1)	4.38	4.38	0.05	

^{a}) Distances (r) and amplitudes (l) in Å. Quantities in parentheses are estimated 2σ uncertainties. Those for distances are assumed the same for all distance types. Quantities in curly brackets were refined as groups. ^{b}) $\tau_1 = \sphericalangle(N_3{-}O_1{-}N{=}O_4)$, $\tau_2 = \sphericalangle(N_2{-}O_1{-}N{=}O_6)$. ^{c}) Distance between average atomic positions. ^{d}) Thermal average distance: $r_g = r_\alpha + K + \delta r$. See [1] for description for N_2O_5. ^{e}) Distance consistent with scattering equations: $r_a = r_g - l^2/r$.

Discussion. – Since the potential functions concern only the torsion-sensitive interatomic distances, it is not surprising that models A and B yield similar values for the short-range structure, *i.e.*, bond distances and bond angles, of N_2O_5. However, as can be seen by the values of the goodness-of-fit factor R, and by the appearance of the

Table 4. *Correlation Matrix for Refined Parameters of N_2O_5*

	σ_{LS} a) b)	r_1	r_2	$\measuredangle_1$	$\measuredangle_2$	V_g	V_a	V_1	l_1	l_2	l_3	l_4	%
r(N–O)	0.0012	100											
⟨r (N=O)⟩	0.0003	– 25	100										
$\measuredangle$(N–O–N)	0.53	22	3	100									
⟨$\measuredangle$(O_1–N=O)⟩	0.079	5	19	24	100								
V_{gear}	1.9	– 6	4	– 7	9	100							
$V_{antigear}$	8.6	16	– 10	17	2	– 97	100						
V_{linear}	8.7	– 10	7	– 12	4	99	– 99	100					
l(N–O)	0.0018	– 16	35	– 7	2	18	– 22	19	100				
l(N=O)	0.0003	– 7	19	2	< 1	1	– 4	2	31	100			
l(N · N) c)	0.0009	– 15	18	< 1	– 42	5	– 8	7	23	32	100		
l(N · O) c)	0.0066	– 4	4	2	– 11	– 32	28	– 31	18	5	10	100	
% Impurity	0.014	13	– 57	– 12	– 8	4	– 1	3	– 38	– 28	– 34	– 5	100

a) Distances (r) and amplitudes (l) in Å, angles ($\measuredangle$) in degrees, potential constants (V) in kcal/mol. b) Standard deviations from least squares refinement. c) Group amplitudes; see *Table 3*.

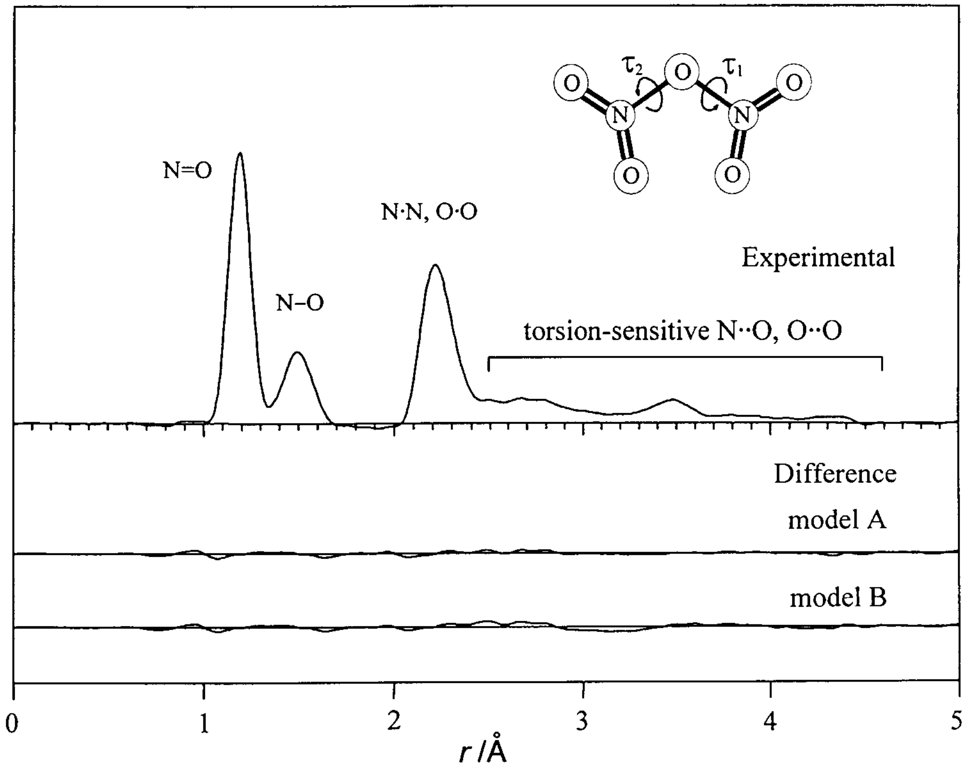

Fig. 5. *Radial distribution of interatomic distances.* The difference curves are experimental minus theoretical.

intensity and radial-distribution-difference curves, our preferred model A with refined values for the potential constants produces a somewhat better fit to the electron-diffraction data than does model B in which these constants were fixed. (This is not

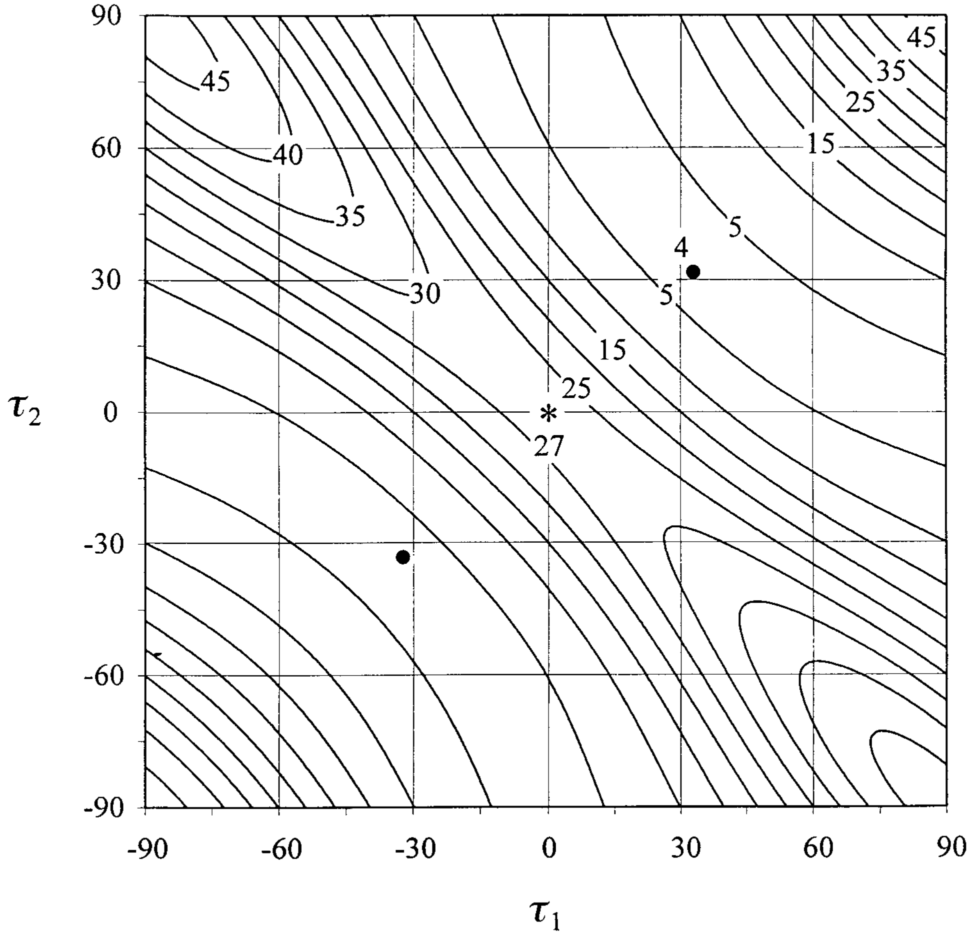

Fig. 6. *Potential surface obtained with use of potential constants from this work.* Potential minima are indicated by black dots, the asterisk at $\tau_1 = \tau_2 = 0°$ indicates a saddle point.

surprising since refinement of these quantities could hardly produce a poorer fit, and, in any case, the fixed values are only rough guesses by *Grabow et al.*) Because both models were based on a set of pseudoconformers characterized by fixed values of the torsion angles, the results do not include a direct measurement of the structural parameters for the conformation of minimum energy. However, it is possible to deduce 'experimental' parameter values for the minimum-energy conformation by first evaluating its torsion angles and then interpolating between parameter values for the two pseudoconformers with torsion angles that bracket those of this conformation. The following illustrates the procedure for the N–O–N bond angle. The minimum-energy conformation is that with $\tau_1/\tau_2 = 33.7/33.7$, found by interpolation of the energy along the line $\tau_1 = \tau_2$. The two pseudoconformers nearest this are thus the reference form with $\tau_1/\tau_2 = 30/30$ and the form with $\tau_1/\tau_2 = 45/45$. The theoretical value for the N–O–N bond angle is predicted to be 4.06° smaller for $\tau_1/\tau_2 = 45/45$ than for $\tau_1/\tau_2 = 30/30$, which was refined to be 113.4(15)°. The interpolated estimate for the experimental value of $\measuredangle(\mathrm{N-O-N})$ for the minimum energy form is then 112.3(15)°. Similar interpolations for the other parameters lead to the values given in *Tables 2* and *3* for model A. The torsion angle(s) of our minimum-energy form (33.7°) is slightly greater than the rough 30° found in our previous work, but considerably less than the 41° suggested by *Grabow et al.* from their MW study. Also, the N–O–N bond angle in our minimum-energy form (112.3°) differs significantly from the suggested 120.5° by *Grabow et al.* The optimized values for these angles from B3LYP/6-311 + G* theory are 30.5° and 114.6°.

The models for the N_2O_5 system in the current study are more elaborate and presumably more realistic than that used in our earlier study because, unlike the earlier study in which C_{2v} symmetry was assumed for the $O-NO_2$ groups, the models allow for variation in the bond distances and bond angles with change in the torsion angles. However, the results for the conformational *averages* of the bond distances and bond angles differ very little from the previous results. The values (r_g) for the system from the present (model A, minimum-energy conformation) and previous analyses are $r(\mathrm{N-O}) = 1.505(4)$ Å and 1.495(4) Å, $\langle r(\mathrm{N=O})\rangle = 1.188(1)$ Å and 1.188(2) Å, $\measuredangle(\mathrm{N-O-N}) = 112.3(15)°$ and 111.8(16)°, and $\measuredangle(\mathrm{O=N=O}) = 134.2(4)°$ and 133.2(6)°. An interesting feature of the present model is the structure of the $O-NO_2$ groups, which differs from the C_{2v} symmetry assumed in the original study. As *Table 2* shows, the angle between the plane of the NO_2 group and the O–N single bond is *ca.* 5° and the two nonequivalent O–N=O angles differ by *ca.* 6°.

Despite the better agreement offered by model A, the potential surface for this model (*Fig. 6*) has little quantitative value because of the very large uncertainties associated with the refined values of the potential constants. Although we believe that the listed uncertainties are poor expressions of the true uncertainties due to the nonlinearity of the problem, even at much smaller values they would clearly allow large changes in the values of the potential constants. For example, even at a small fraction of their listed values, they would encompass not only the fixed values of model B, but permit zero values for all potential constants. The latter circumstance is absurd: it corresponds to equal energy for all pseudoconformers, which is excluded by all previous experimental and theoretical work. The existing large uncertainties derive from the fact that electron diffraction simply cannot produce accurate values of the conformational composition of a system such N_2O_5. The reason is that the amounts of conformers with energies 1–2 kcal/mol greater than the most stable one are too small to be measured reliably: at 1 kcal/mol, they are present at less than 19% at room temperature and at 2 kcal/mol less than 4%. The result is that any evaluation of a potential function from electron diffraction depends almost entirely on data near the minima of the function and cannot be expected to yield values near saddle points or maxima having values of several kcal/mol. This is the explanation of large difference in the scales of the potential surfaces corresponding to the refined and fixed values of the potential constants seen in *Figs. 5* and *6*.

Despite the very different coefficients for the potential function terms in model A and B, they give nearly the same values for the torsion angles of the most stable pseudoconformer – slightly greater than 30° for a species of C_2 symmetry. Further, in those portions of the potential-energy surface that are most important for a GED study, the two potential surfaces are similar. Both indicate that the molecule undergoes large amplitude torsional motions and agree well on the values of the important parameters as well as on those from our previous GED [1] results. They are also in good agreement with the IR [4–6][5] and MW [6][8] results and the previously reported theoretical calculations [9][10][12]. Both surfaces indicate a relatively low energy barrier for interconversion to the equivalent minimum-energy structure having negative torsion angles *via* a path that includes the $\tau_1/\tau_2 = 0/90$ structure: for model A, the barrier is *ca.* 0.26 kcal/mol, whereas for model B, the barrier is *ca.* 0.02 kcal/mol. Where the two models differ significantly is in regions of the potential-energy surface where the potential energy is high. For example, the barrier for interconversion to the equivalent low-energy structure having negative torsion angles through any other path than *via* the $\tau_1/\tau_2 = 0/90$ structure is found to be extremely high in model A: the lowest barrier alternative path requires some 23 kcal/mol to reach a saddle point at $\tau_1/\tau_2 = 0/0$. In model B, the barrier is a much more reasonable 2.0 kcal/mol for this interconversion path.

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