

THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES

Part IV. An ab initio study of hydrazoic acid, azidomethane, azidoethane, azidoethene and azidomethanal*

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(Received 19 September 1986)

ABSTRACT

Fully optimized geometries have been calculated for the title compounds at the Hartree-Fock SCF level and compared with existing experimental data. A basis set of double zeta quality has been employed. For hydrazoic acid, a calculation with a larger basis set, expected to give results near the Hartree-Fock limit, has also been performed. All of the calculations show the azide group to be slightly bent with a *trans* configuration around the central NN bond. Azidoethane is predicted to exist in two conformations, *gauche* (71°) and *anti*, with a negligible energy difference of 0.26 kJ mol^{-1} between them. Azidoethene and azidomethanal both prefer the *syn* orientation of the azide group with respect to the C=C or C=O bonds, the computed energy difference between the *anti* and *syn* conformations being 3.31 and 30.3 kJ mol^{-1} , respectively.

The barrier to rotation around the C-N bond has been calculated to be 3.75 kJ mol^{-1} in azidomethane while in azidoethane it was 3.30 and 9.40 kJ mol^{-1} in the eclipsed *anti-clinal* (120°) and *syn* positions, respectively.

Complete harmonic force fields and dipole moment derivatives have been calculated for hydrazoic acid, azidomethane and for the two stable conformations of azidoethane. For azidoethane and azidomethanal only the azide part of the harmonic force field has been calculated. The theoretical harmonic force fields have been modified through scaling by a least squares refinement to the observed wavenumbers of hydrazoic acid, azidomethane and azidoethane (*anti* and *gauche*). Infrared vapour phase intensities have been calculated and theoretical spectra are presented for azidomethane and azidoethane.

INTRODUCTION

Early investigations of the molecular structures of organic covalent azides in the vapour phase, as for instance methyl azide [1], reported a linear azide group with a shorter terminal and a longer middle NN bond. An X-ray study of the crystal structure of cyanuric triazide [2] also reported a linear N-N-N chain, although a small deviation from linearity could not be ruled out.

*Part III of this series is given as ref. 11.

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More recent investigations of hydrazoic acid [3], methyl azide [4] and vinyl azide [5] by microwave spectroscopy, as well as an electron diffraction study of methyl azide [6], all retain the assumption of a linear azide configuration.

A subsequent electron diffraction analysis of gaseous cyanogen azide [7], on the other hand, made no such assumption and determined the N—N—N angle to be 175.3° . Later, a reinvestigation of the microwave spectra of hydrazoic acid [8] also concluded that the azide chain is non-linear, and electron diffraction measurements performed in this laboratory on a series of organic azides [9–11] all indicate that the azide group is slightly bent, with a *trans* configuration around the middle NN bond.

Two more recent *ab initio* calculations on HN_3 [12, 13] both confirm the non-linear geometry, and a combined electron diffraction and *ab initio* study of propargyl azide [14] presents the same conclusion.

In order to investigate the structures and preferred conformations of both saturated and olefinic azides, quantum chemical calculations were performed on hydrazoic acid (HN_3), azidomethane (methylazide, hereafter designated MeN_3), azidoethane (EtN_3) and azidoethene (vinylazide, VN_3).

Very little is known about the conformational properties of the industrially important acyl azides, R—CO—N_3 . Microwave studies of methyl azidoformate (CH_3OCON_3) [15] and ethanoyl azide (acetyl azide, CH_3CON_3) [16] indicate that the azide group prefers the *syn* position with respect to the carbonyl group, and a calculation on the model compound azido-methanal (formyl azide, FoN_3) was also carried out.

COMPUTATIONAL DETAILS

In order to compute the equilibrium structures and harmonic force fields of the various azides, Hartree—Fock level calculations were performed using a gradient version of the program MOLECULE [17, 18]. The geometry relaxation was continued until all Cartesian forces on the atomic coordinates were less than 0.001 a.u.

A $7s3p$ basis set developed for the first row atoms [19] has proved its merit as a medium-sized basis set able to give equilibrium geometries in good agreement with experimental values. This set was therefore chosen as a starting set for carbon, nitrogen and oxygen. For hydrogen, a $4s$ primitive set [20] was employed and the primitive sets were contracted to double zeta quality, $4s2p$ on C, N and O, and $2s$ on H, the orbital exponents on hydrogen being scaled by a factor of $(1.2)^2$ [21]. This basis set is hereafter referred to as DZ.

In order to test the effect of a larger basis set flexibility on the computed azide geometries and force constants, a series of calculations were carried out on HN_3 using a relatively large basis set, expected to give results near the Hartree—Fock limit. A primitive $10s6p$ set [20] was chosen for nitrogen, which was contracted to $5s4p$ [22] and augmented by a set of *d*-functions

with exponent $\zeta = 0.95$. For hydrogen a 5s set [20] contracted to 3s was employed. The hydrogen *s*-exponents were scaled by a factor of $(1.49)^2$ [22] and a set of *p*-orbitals with exponent $\zeta = 0.80$ was added to the 3s set. This basis set is hereafter referred to as HF.

The force constants were calculated by numerical differentiation of the gradient vector in a number of distorted geometries. The bond lengths and angles were displaced ± 2.5 pm and $\pm 2^\circ$ from their equilibrium values. For the torsional coordinates, an 8° deviation from equilibrium was chosen.

By-products of the calculations are the dipole moment derivatives with respect to the internal coordinates. The dipole moment derivatives were calculated by numerical methods imposing the Eckart conditions on the individual molecules during the deformation of the bond lengths or angles.

RESULTS AND DISCUSSION

Geometries

The computed equilibrium azide geometries are shown in Figs. 1–5 and the calculations were all consistent with a slightly bent azide structure having a shorter terminal NN distance and a *trans* configuration around the middle NN bond. All structures were optimized and the computed energy difference between the conformers is listed in the figure captions. The structural parameters of the azide group are collected in Table 1, with the available experimental values included for comparison.

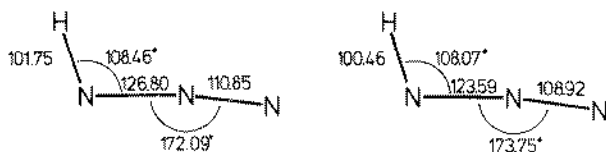


Fig. 1. The *ab initio* molecular structure of hydrazoic acid (HN_3): (left) Double zeta basis, computed energy: -163.583218 hartree. (right) Near-Hartree-Fock limit basis, computed energy: -163.895796 hartree. Bond lengths in pm and angles in degrees.



Fig. 2. The *ab initio* molecular structures of azidomethane (CH_3N_3): double zeta basis, computed energies, -202.567219 hartree (staggered) and -202.565796 hartree (eclipsed); units, see Fig. 1; ΔE (eclipsed–staggered) = 3.30 kJ mol $^{-1}$.

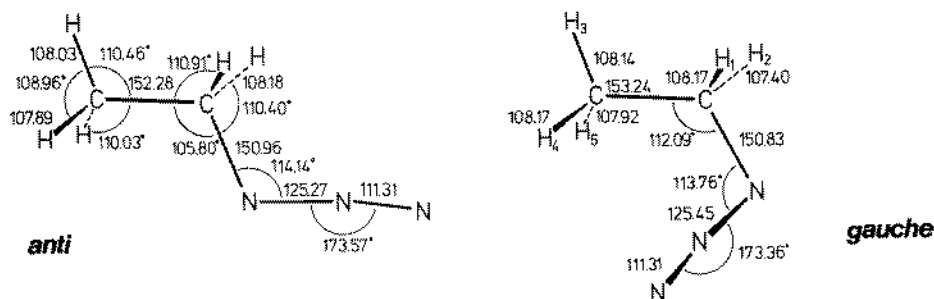


Fig. 3. The ab initio molecular structures of azidoethane ($\text{CH}_3\text{CH}_2\text{N}_3$): double zeta basis; computed energies, -241.559431 hartree (*anti*) and -241.559334 hartree (*gauche*); units, see Fig. 1; ΔE (*gauche-anti*) = 0.26 kJ mol^{-1} . Additional bond angles for the *gauche* conformer: $\angle\text{NCH}_1 = 110.71^\circ$, $\angle\text{NCH}_2 = 103.41^\circ$, $\angle\text{CCH}_1 = 111.17^\circ$, $\angle\text{CCH}_2 = 110.78^\circ$, $\angle\text{H}_1\text{CH}_2 = 108.37^\circ$, $\angle\text{CCH}_3 = 110.42^\circ$, $\angle\text{CCH}_4 = 111.14^\circ$, $\angle\text{CCH}_5 = 109.95^\circ$, $\angle\text{H}_3\text{CH}_4 = 107.99^\circ$, $\angle\text{H}_3\text{CH}_5 = 108.78^\circ$, $\angle\text{H}_4\text{CH}_5 = 108.49^\circ$, NNCH_1 torsion = 71.29° , NCCH_3 torsion = 175.31° .

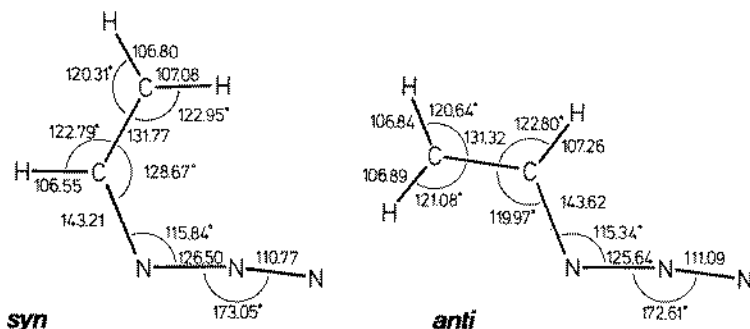


Fig. 4. The ab initio molecular structures of azidoethene (CH_2CHN_3): double zeta basis; computed energies, -240.378044 hartree (*syn*) and -240.376783 hartree (*anti*); units, see Fig. 1; ΔE (*anti-syn*) = 3.31 kJ mol^{-1} .

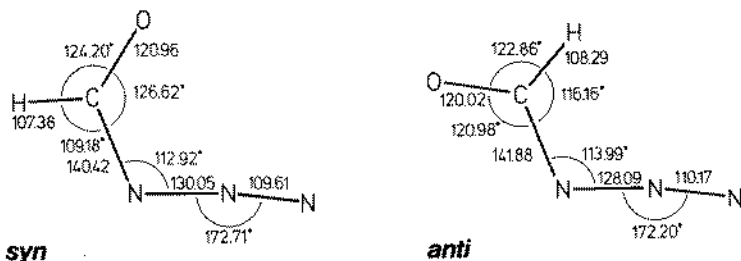


Fig. 5. The ab initio molecular structures of formyl azide (CHON_3): double zeta basis; computed energies, -276.153270 hartree (*syn*) and -276.141740 hartree (*anti*); units, see Fig. 1; ΔE (*anti-syn*) = 30.3 kJ mol^{-1} .

TABLE 1

Structure (pm, degrees) and gross atomic charges (e) of the azide group in some organic azides

$N_1 \equiv N_3 = N_2 - X$	N≡N	N=N	N-X	N≡N=N	N=N-X	Gross atomic charge				Σq_A	$r_{N \equiv N} / r_{N=N}$
						q_1	q_2	q_3	q_X		
HN ₃											
DZ ^a	110.9	126.8	101.8	172.1	108.5	+0.053	-0.090	-0.290	+0.327	-0.327	0.874
HF	108.9	123.6	100.5	173.8	108.1	-0.045	+0.235	-0.408	+0.218	-0.218	0.881
exp ^b	113.4(2)	124.3(5)	101.5(15)	171.3(50)	108.8(40)						
CH ₃ N ₃ (MeN ₃)											
DZ ^a	111.2	125.6	150.3	174.0	112.6	+0.044	-0.070	-0.282	-0.325	-0.308	0.885
exp ^c	113.0(5)	121.6(4)	146.8(5)	180 ^d	116.8(3)						
CH ₃ CH ₂ N ₃ (EtN ₃)											
<i>Anti</i> DZ	111.3	125.3	151.0	173.6	114.1	+0.047	-0.071	-0.281	-0.195	-0.305	0.889
<i>Gauche</i> DZ	111.3	125.5	150.8	173.4	113.8	+0.041	-0.068	-0.273	-0.200	-0.300	0.887
HCCCH ₂ N ₃											
<i>Gauche</i> DZ ⁱ	111.1	125.7	151.2	172.6	114.8						0.884
exp ^e	113.7(6)	124.9(7)	146.4(13)	169.2(41)	114.5						
CH ₂ CHN ₃ (VN ₃)											
<i>Syn</i> DZ	110.8	126.5	143.2	173.1	115.8	+0.090	-0.051	-0.299	+0.045	-0.260	0.876
exp ^f	114.3(4)	125.3(6)	143.4(7)	176.5(35)	116.8(11)						
exp ^g	114.1(9)	124.2(12)	143.2(24)	166.7(56)	114.5(23)						
<i>Anti</i> DZ	111.1	125.6	143.6	172.6	115.3						
CHON ₃ (FoN ₃)											
<i>Syn</i> DZ	109.6	130.1	140.4	172.7	112.9	+0.151	-0.020	-0.336	+0.491	-0.205	0.843
exp ^h	113.1	124.8	146.0	180 ^d	110.7						

^aDZ and HF refer to basis sets; see computational details. ^bFrom ref. 8. ^cFrom ref. 6. ^dAssumed. ^eFrom ref. 14. ^fStructural parameters from 2-azido-1,3-butadiene, ref. 10. ^gStructural parameters from 2,3-diazido-1,3-butadiene, ref. 11. ^hStructural parameters from methyl azidoformate, CH₃OCON₃, ref. 15. ⁱFrom ref. 14.

The calculations show that the preferred conformation of MeN₃ is staggered with a rotational barrier of 3.75 kJ mol⁻¹. This result is in good agreement with the experimental value, $V_3 = 2.98 \pm 0.09$ kJ mol⁻¹, from the microwave investigation [4].

The conformation of EtN₃ is obviously also staggered, either *gauche* or *anti*. As seen in Table 2, the computed energy difference between the most stable, *anti*, and the less stable, *gauche*, conformation is negligible. The accuracy of the conformational energy differences, calculated at the Hartree-Fock level with the DZ basis set, is probably 1–1.5 kJ mol⁻¹, and preliminary results from an IR matrix isolation study of EtN₃ indicate an energy difference of ca. 0.6 ± 0.1 kJ mol⁻¹ in the nitrogen matrix, with the *gauche* conformation as the more stable [23].

In order to determine the barriers to rotation around the C–N bond, two additional EtN₃ structures were refined: the eclipsed *anticlinal* conformer with the azide group rotated 120° away from the methyl group and the sterically unfavorable *syn* arrangement. A selected set of EtN₃ structural parameters and their variation with the C–N torsional angle are given in Table 2, and the C–N torsion potential energy function, expanded to third order in $\cos\theta$ is also presented.

It appears from our calculations that the two unsaturated azides, VN₃ and FoN₃, both prefer a *syn* orientation of the azide group with respect to the adjacent C=C and C=O bonds. The computed energy difference between the *anti* and *syn* conformers of VN₃ is 3.31 kJ mol⁻¹, in reasonable agreement with the result, 1.9 ± 0.4 kJ mol⁻¹, from relative intensity measurements by microwave spectroscopy [5]. The only experimental structure parameters of vinylic azides come from recent electron diffraction studies of 2-azido-1,3-butadiene [10] and 2,3-diazido-1,3-butadiene [11]. These results

TABLE 2

Calculated variation of the ethyl azide structure with the C–N conformation (r in pm)^a

Dihedral angle	0° (<i>syn</i>)	71.29° (<i>gauche</i>)	120° (<i>synclinal</i>)	180° (<i>anti</i>)
r _{N≡N}	111.66	111.31	111.49	111.31
r _{N=N}	124.25	125.45	124.77	125.27
r _{N-X}	151.37	150.83	151.17	150.96
N=N≡N	172.94°	173.36°	173.69°	173.57°
N=N–C	116.89°	113.76°	114.95°	114.14°
N–C–C	116.56°	112.09°	108.61°	105.80°
Energy (hartree)	-241.555852	-241.559334	-241.558174	-241.559431
ΔE (kJ mol ⁻¹)	9.40	0.26	3.30	0.0

^aThe C–N torsional potential $V(\theta) = V_0 + V_1 \cos\theta + V_2 \cos 2\theta + V_3 \cos 3\theta$ where $V_0 = 2.928(83)$ kJ mol⁻¹; $V_1 = 2.226(94)$ kJ mol⁻¹; $V_2 = 1.734(88)$ kJ mol⁻¹; $V_3 = 2.470(68)$ kJ mol⁻¹.

have been included in Table 1 for a comparison with the theoretical structure parameters of *syn* azidoethene.

For FoN_3 the *anti-syn* energy difference is calculated to be 30.3 kJ mol^{-1} , which agrees with the observation of only one conformer in the microwave spectra of both CH_3OCON_3 [15] and CH_3CON_3 [16]. The r_0 -structure of the azide group in CH_3OCON_3 [15] is presented with the theoretical structure of FoN_3 in Table 1. Apparently, the basis set employed in our calculations on polar compounds, such as FoN_3 , is inadequate, but we are nevertheless confident that the acyl azides in general exist in the C—N *syn* conformation only. This conclusion may be significant for understanding the photolytic and thermal decomposition and the rearrangement of acyl azides to isocyanates.

As apparent from Table 1, the double zeta basis yields computed N—X and N=N distances which are larger than the experimental values, whereas in the Hartree—Fock limit shorter equilibrium bond lengths are, in fact, expected. These systematic deviations, and similar trends in the force constants, harmonic frequencies and charge distributions, lead to the conclusion that the double zeta basis does not provide a near Hartree—Fock limit description of the azide group.

In spite of the systematically longer N=N and N—X bond lengths computed, the calculated moments of inertia agree very well with the available observations [4, 5, 24], generally within 1–2% as apparent from Table 3. However, the *syn* conformer of VN_3 departs from this rule, believed to be due to the exceptionally large computed N=N—C angle, 128.67° . Indeed, a far better agreement with the experimental moments of inertia is obtained with a value of 125° , but it is not known whether the large N=N—C angle is a computational artifact or not. It may be noted that the proposed structures for the *syn* and *anti* conformations of VN_3 have very different C—N bond distances [5], which seems unlikely from our calculations. Further calculations, using different basis sets, would have to be carried out before any firm conclusions can be drawn, but this is beyond the scope of this work. However, the HF basis described above was applied to the HN_3 molecule and the resulting N=N and N—H bond lengths are both shorter than the experimental values, as expected when approaching the Hartree—Fock limit.

Trends within the series of azides, however, may still be revealed by the present double zeta calculations, and significant variations in the azide bond lengths were indeed observed. An increasing electronegativity of the substituent group, R, of a covalent azide, R—N_3 , is expected to shorten the R—N bond and to increase the bond length difference between the NN bonds of the azide groups [25]. Table 1 shows how the ratio $r_{\text{N=N}} / r_{\text{N=N}}$ decreases from MeN_3 and EtN_3 to FoN_3 . An estimate of the electronegativity of the R substituent is provided by the calculated total charge of the azide group, and a rough correlation between the total charge and the bond length ratio can be seen in the results of Table 1.

TABLE 3

Comparison between experimental and theoretical moments of inertia ($\text{u}\text{\AA}^2$) of some organic azides

		I_A	I_B	I_C	Ref.
HN ₃	DZ ^a	0.840455	41.9696	42.8101	24
	Exp.	0.8270956	41.995168	42.895904	
CH ₃ N ₃ (MeN ₃)	DZ	12.0846	93.2265	102.171	4
	Exp.	11.498	93.664	102.136	
CH ₂ CHN ₃ (EtN ₃)	<i>Anti</i> DZ	15.8907	200.182	209.877	
	<i>Gauche</i> DZ	38.1580	151.488	174.516	
CH ₂ CHN ₃ (VN ₃)	<i>Syn</i> DZ	33.0434	128.516	161.559	5
	<i>Syn</i> Exp.	34.38346	123.611	158.145	
	<i>Anti</i> DZ	10.7430	183.579	194.322	
	<i>Anti</i> Exp.	10.80759	183.680	194.463	
CHON ₃ (FoN ₃)	<i>Syn</i> DZ	30.6632	122.053	152.716	
	<i>Anti</i> DZ	9.29037	180.008	189.298	

^aDZ refers to double zeta basis: see computational details.

Dipole moments and charge distributions

Previous gross atomic charge calculations on HN₃ [12] and ClN₃ [26] unambiguously show the charge distribution of the azide group to be



As is apparent from Table 1, the present double zeta calculations fail to reproduce this scheme, whereas the larger basis set, applied to the HN₃ molecule, agrees with the previous results. In view of the known deficiencies of the double zeta set, which have been discussed above, it is hardly surprising that the computed charges will be affected like the bond lengths and force constants (see later).

Nevertheless, the computed dipole moments given in Table 4 agree quite well with the experimental values [4, 5, 24, 27, 28]. With the exception of FoN₃, the calculations all show the azide group to be the negatively charged end. The dipole moment vector is invariably directed along the R—N bond, as was pointed out as long ago as 1931 from bulk dipole measurements on a series of phenyl azides [29]. Where experimental data are available, the angle between the experimental and computed dipole moments is found to be about 25°, with the computed moments lying nearer to the

TABLE 4

Observed and calculated dipole moments (D)^a of some organic azides

		$ \mu_a $	$ \mu_b $	$ \mu_c $	$ \mu_{tot} $	Ref.
HN ₃	(DZ) ^b	0.14	1.98	—	1.99	
	(HF)	0.09	1.82	—	1.82	
	Exp.	0.837	1.48	—	1.70	24, 27
CH ₃ N ₃ (MeN ₃)						
	(DZ)	1.50	1.76	—	2.31	
	Exp.	1.91	1.03	—	2.17	4
CH ₃ CH ₂ N ₃ (EtN ₃)						
<i>Anti</i>	(DZ)	1.50	1.69	—	2.26	
<i>Gauche</i>	(DZ)	1.95	0.75	1.14	2.38	
	Exp.				2.12	28
CH ₂ CHN ₃ (VN ₃)						
<i>Syn</i>	(DZ)	1.01	0.93	—	1.37	
	Exp.	1.337	0.326	—	1.376	5
<i>Anti</i>	(DZ)	0.72	1.60	—	1.75	
	Exp.	1.156	0.900	—	1.465	5
CHON ₃ (FoN ₃)						
<i>Syn</i>	(DZ)	0.92	1.25	—	1.55	
<i>Anti</i>	(DZ)	3.14	2.40	—	3.95	

^a1 D = 3.3356.10⁻³⁰ C.m. ^bDZ and HF refer to the basis sets; see computational details.

perpendicular to the NNN chain. This discrepancy is believed to be a correlation effect.

Harmonic force fields and vibrational frequencies

The computed force constants of the azide group are collected in Table 5. It can be seen that the variations in the NN bond lengths are also reflected in the diagonal stretching force constants. As was mentioned above, the calculated N=N and N-X bond lengths are too long, and consequently the corresponding stretching force constants were found to be too small. Complete force fields were only computed for HN₃, MeN₃ and the *gauche* and *anti* conformations of EtN₃; some preliminary results dealing with HN₃ and MeN₃ have been published elsewhere [30].

The too low N=N and N-X stretching frequencies [30] (see also Tables 6-9) are believed to be caused by an insufficient basis set flexibility, giving too weak bonds and too long bond distances. A calculation performed on HN₃ with the HF basis set yielded shorter bond lengths and significantly higher N=N and N-H stretching force constants. The resulting frequencies are all higher than the observed values, as expected of a near-Hartree-Fock limit wavefunction, but, surprisingly, the bending modes are slightly lower than their double zeta counterparts. However, the larger basis confirms

TABLE 5

Valence force fields^a for the azide group, ab initio results, double zeta basis

N ₃ -R constant	-H ^b	-H	-CH ₃	-CH ₂ CH ₃		-CH=CH ₂	-CHO
				<i>Anti</i>	<i>Gauche</i>		
N≡N	25.428	22.500	21.840	21.656	21.713	22.571	25.098
N≡N/N=N	2.353	2.362	2.420	2.429	2.422	2.283	1.902
N≡N/N-X	-0.198	-0.136	-0.147	-0.171	-0.173	-0.363	-0.611
N=N/N≡N=N	0.091	-0.056	-0.097	-0.088	-0.091	-0.112	-0.059
N≡N/N=N-X	-0.021	-0.058	-0.154	-0.144	-0.133	-0.204	-0.256
N=N	9.570	7.238	7.660	7.894	7.745	7.191	5.320
N=N/N-X	0.059	-0.010	0.230	0.215	0.276	0.563	0.864
N=N/N≡N=N	0.282	0.287	0.303	0.307	0.334	0.343	0.288
N=N/N=N-X	0.941	1.171	1.097	1.038	1.059	1.163	1.319
N-X	7.721	6.746	4.506	4.326	4.371	5.389	5.685
N-X/N≡N=N	0.015	-0.025	-0.003	-0.019	-0.027	-0.037	-0.063
N-X/N=N-X	0.275	0.338	0.719	0.625	0.681	0.816	0.634
N≡N=N	0.693	0.792	0.792	0.798	0.798	0.763	0.640
N≡N=N/ N=N-X	0.102	0.089	0.139	0.135	0.138	0.148	0.151
N=N-X	1.016	1.127	1.367	1.255	1.308	1.447	1.492
τ _{N=N}	0.00975	0.0175	0.0108	0.0116	0.0122	0.0127	0.0132

^aUnits: stretch and stretch/stretch, mdyn/Å; stretch/bend, mdyn/rad; bend and bend/bend, mdyn Å/rad². ^bLarge basis set (HF); see computational details.

TABLE 6

Observed and calculated fundamental frequencies [cm⁻¹] and IR intensities [km mol⁻¹] of hydrazoic acid (H¹N₃)

Observed ^a	Calculated DZ ^b					Calculated HF					Description
	Harm.	Scaled	Intensity			Harm.	Scaled	Intensity			
			a	b	c			a	b	c	
A'											
3336 m	3488	3336	9.5	0.8	—	3731	3336	37.7	18.7	—	N-H stretch
2129 vs	2330	2132	392.9	0.1	—	2502	2129	659.2	1.1	—	N≡N stretch
1264 m	1465	1263	53.7	1.2	—	1428	1263	4.9	0.8	—	N=N-H bend
1151 vs	1026	1152	214.5	2.7	—	1228	1149	292.1	0.4	—	N=N stretch
537 w	599	531	17.7	1.3	—	569	533	17.6	3.8	—	N≡N=N bend
A''											
606 w	683	603	—	—	0.8	657	601	—	—	1.8	N=N torsion

^aFrom refs. 33-49: relative intensities (w, m, vs) from ref. 34. ^bDZ and HF refer to basis sets; see computational details.

TABLE 7

Observed and calculated fundamental frequencies [cm^{-1}] and IR intensities [km mol^{-1}] of methyl azide (Me^{14}N_3)

Observed ^a	Calculated		Intensity			Description ^d
	Harm.	Scaled				
			a	b	c	
A'						
3023 m,A	3357	3055	8.6	6.9	—	CH ₃ asym. stretch
2935 s,A	3188	2901	21.6	18.3	—	CH ₃ sym. stretch
2106 vs,A	2288	2106	572.7	24.8	—	N≡N stretch
1456 m,A	1661	1467	24.1	3.7	—	CH ₃ asym. def.
1417 m,A	1602	1448	8.0	0.6	—	CH ₃ sym. def.
1272 vs,A	1205	1279	184.9	0.7	—	N=N stretch
1132 m,A	1254	1123	8.2	1.2	—	CH ₃ rock
910 m,B	890	908	0.4	8.3	—	N—C stretch
666 m,A	745	660	8.8	0.0	—	N≡N=N bend
245 m,A	291	249	6.1	0.1	—	N=N—C bend
A''						
2962 s,C	3247	2956	—	—	41.3	CH ₃ asym. stretch
1465 m,C	1665	1467	—	—	32.8	CH ₃ asym. def.
1087 ^b vw,C	1186	1069	—	—	6.1	CH ₃ rock
560 m,C	712	561	—	—	16.2	N=N torsion
100 ^c	135	100	—	—	0.5	CH ₃ torsion

^aFrom refs. 41–43: relative intensities (vw, m, s, vs) and band types (A, B, C) from ref. 44. ^bFrom ref. 44. ^cFrom ref. 4 (calculated using a torsional barrier of 2.98 kJ mol⁻¹). ^dKey: asym., asymmetric; sym., symmetric; def., deformation.

the validity of the double zeta force field, with the exception of the diagonal stretchings and a few small off-diagonal terms mentioned above. All the important interaction constants are calculated to be almost equal using the two basis sets, especially the very large N≡N/N=N and N=N/N=N—X interaction constants (see later).

The higher values for the frequencies calculated from a Hartree–Fock limit wavefunction can be partly attributed to the neglect of anharmonicity, and partly to an overestimation of the harmonic force constants owing to basis set truncation and the neglect of electron correlation [31]. The effect of anharmonicity can be compensated by introducing cubic and higher terms in a perturbation treatment of the vibrational problem, but the computational effort required increases rapidly with the number of internal coordinates. Not only is the perturbation procedure a cumbersome task, but a large number of additional calculations of the energy gradient have to be performed in order to determine all the cubic and higher order force constants (see later).

The aim of the present study was to yield a set of azide force fields which can be used in the assignment of vibrational spectra, and a different ap-

TABLE 8

Observed and calculated fundamental frequencies [cm^{-1}] and IR intensities [km mol^{-2}] of *anti* azidoethane (Et^{14}N_3)

Observed ^a	Calculated		Intensity			Description
	Harm.	Scaled				
			a	b	c	
A'						
(2995)	3282	2988	7.4	23.8	—	CH ₃ asym. stretch
(2942)	3214	2926	22.5	0.1	—	CH ₃ sym. stretch
(2910)	3188	2901	0.5	29.6	—	CH ₂ sym. stretch
2114	2282	2106	648.7	8.8	—	N≡N stretch
1471	1672	1490	18.2	1.1	—	CH ₂ scissor
1460	1664	1463	1.3	6.5	—	CH ₃ asym. def.
1388	1574	1389	4.4	1.4	—	CH ₃ sym. def.
1345	1506	1334	27.6	1.0	—	CH ₂ wag
1280	1198	1298	254.2	0.4	—	N=N stretch
1124	1245	1116	0.8	3.2	—	CH ₃ rock
1022	1055	1023	2.1	5.1	—	C—C stretch
857	891	854	0.6	2.6	—	N—C stretch
630	699	633	9.9	0.0	—	N≡N=N i.p. bend
390	419	394	10.5	0.4	—	N—C—C bend
—	217	190	0.6	0.0	—	N=N—C bend
A''						
(2998)	3295	2999	—	—	27.7	CH ₃ asym. stretch
(2929)	3228	2938	—	—	39.5	CH ₂ asym. stretch
1450	1646	1444	—	—	19.7	CH ₃ asym. def.
1244	1419	1259	—	—	0.5	CH ₁ twist
1107	1259	1105	—	—	17.9	CH ₂ /CH ₂ rock
807	873	803	—	—	1.0	CH ₂ /CH ₃ rock
562	679	565	—	—	18.7	N=N torsion
—	252	225	—	—	4.7	CH ₃ torsion
—	56	42	—	—	1.4	C—N torsion

^aPreliminary results from ref. 23, frequencies from N₂ matrix IR spectra. Values in parentheses have not been included in the least squares adjustment.

proach, based on the introduction of empirical scale factors [31, 32], was employed. The computed harmonic force constants, F_{ij} , were adjusted according to the scheme

$$F'_{ij} = (x_i x_j)^{1/2} F_{ij} \quad (1)$$

where F'_{ij} is the scaled force constant and x_i , x_j are scale factors for the diagonal force constants F_{ii} and F_{jj} , respectively. Force constants related to the same type of internal coordinates share the same scaling factor; i.e., all the C—H stretching constants are grouped together, all the HCH bending constants are grouped together, etc. We made no effort to use special combinations of valence coordinates as advocated by Pulay et al. [32], as we

TABLE 9

Observed and calculated fundamental frequencies [cm^{-1}] and IR intensities [km mol^{-1}] of *gauche* azidoethane (Et^{14}N_3)

Observed ^a	Calculated			Description		
	Harm.	Scaled	Intensity			
			a	b	c	
A						
(2995)	3323	3025	8.7	11.4	4.0	CH_2 asym. stretch
(2942)	3282	2988	1.1	0.1	22.4	CH_2 asym. stretch
(2950)	3255	2964	22.3	3.0	0.9	CH_3 asym. stretch
(2950)	3207	2919	4.6	1.8	26.1	CH_2 sym. stretch
(2910)	3197	2910	3.0	18.2	4.1	CH_2 sym. stretch
(2100)	2283	2104	510.2	104.7	6.3	$\text{N}\equiv\text{N}$ stretch
1465	1670	1488	1.5	0.7	3.1	CH_2 scissor
1453	1665	1460	4.2	1.1	0.1	CH_2 asym. def
1450	1660	1459	2.8	5.0	7.2	CH_2 asym. def.
1382	1568	1384	2.4	8.0	1.8	CH_2 sym. def.
1341	1506	1337	15.1	2.7	0.1	CH_2 wag
(1280)	1217	1292	172.9	9.1	0.1	$\text{N}=\text{N}$ stretch
(1244)	1436	1253	34.2	5.5	0.0	CH_2 twist
1140	1266	1124	5.6	1.6	0.4	CH_3/CH_2 rock
1082	1184	1081	3.4	1.2	5.6	CH_3 rock
989	1007	989	5.0	3.8	1.0	C—C stretch
844	855	847	0.0	1.6	0.7	C—N stretch
799	923	807	0.6	0.5	2.7	CH_2/CH_3 rock
657	734	656	8.5	1.8	0.0	$\text{N}\equiv\text{N}=\text{N}$ i.p. bend
564	675	561	2.4	8.9	15.8	$\text{N}=\text{N}$ tors
408	426	405	0.1	4.1	0.9	C—N—N bend
—	293	260	3.2	0.0	0.5	C—N—N bend/ CH_3 torsion
—	199	179	1.4	0.0	0.2	C—N—N bend/ CH_3 torsion
—	78	58	0.3	0.5	1.6	C—N torsion

^aPreliminary results from ref. 23, frequencies from N_2 matrix IR spectra. Values in parentheses have not been included in the least squares adjustment.

feel that this reduces the credibility of the method. The values of the factors are determined by a least squares fitting to the observed frequencies.

Among the azides studied here, only HN_3 [33–40], MeN_3 [41–44] (and older references) and EtN_3 [23, 45] have been studied by vibrational spectroscopy. Unfortunately, only the spectra and not the wavenumbers of the observed bands of $\text{CH}_3\text{CH}_2\text{N}_3$ and $\text{CD}_3\text{CD}_2\text{N}_3$ are given in ref. 45. The infrared and Raman spectra of EtN_3 are currently being interpreted in detail [23] and only preliminary results have been available in the present study.

The scaling procedure outlined was first tested with the spectroscopic data on HN_3 [33–40]. It was not possible to get any reasonable agreement with the observations by scaling the force field obtained with the DZ basis set unless a separate scale factor was applied to the large off-diagonal term

coupling the N=N stretching and N=N-H bending coordinates of HN₃. Previous experience has shown that this is often necessary with large coupling force constants or terms connecting near-degenerate, zeroth-order frequencies [31]. On the other hand, when the same scaling procedure was applied to the force field obtained with the HF basis set, no separate scaling factor was necessary.

A comparison between the unscaled force constants (Table 5) obtained with the two different basis sets reveals why it is necessary to scale the N=N/N=N-X interaction constant in the "DZ" force field separately. The N=N force constant is overestimated using the HF basis but underestimated with the DZ basis, while the interaction constants, as mentioned before, are calculated to be almost the same with the two basis sets. This, in turn, results in a down-scaling of all "HF" force constants connected with the N=N stretching coordinate but in upscaling of the corresponding "DZ" force constants. The result of introducing an extra scaling factor for the N=N/N=N-X interaction constant in the adjustment of the "DZ" force field is that the scaled value of this constant ends up almost equal to the scaled value in the corresponding "HF" force field. This interesting result leads to the bold assumption that some similar scaling should be used for all the force constants connected with the N=N stretching coordinate. Assuming equal values for the scaled "HF" and "DZ" constants N=N/N=N and N=N/N=N-X leads to a scaling factor $x_{N=N} = 0.70$ for the off-diagonal terms.

A common set of 19 scale factors was adjusted by a least squares procedure to more than 80 observed frequencies and isotopic shifts of HN₃ (six isotopic species), MeN₃ (two isotopic species) and EtN₃ (two conformers). The spectroscopic data were weighted by σ_i^{-2} , where σ_i was taken as 1% of the observed vibrational frequencies, but not less than 5 cm⁻¹. The scaling factor for the N=N torsional constants had to be treated separately for HN₃, MeN₃ and EtN₃ in order to obtain a satisfactory agreement between observed and calculated fundamental frequencies. The scaling factor, $x_{N=N}$, for the off-diagonal terms, $F_{N=N,j}$, was constrained to the value 0.70 derived above.

The scaled azide force fields and the scale factors applied are shown and compared with "experimental" force constants for HN₃ [35, 46] and MeN₃ [46] in Table 10. The variation of the force constants from HN₃ through MeN₃ to EtN₃ can easily be rationalized in terms of σ -electron donation from the substituted group. Since the computed force fields for the azide group in the *anti* and *gauche* conformations of EtN₃ are almost identical we give only the scaled force field of the *anti* conformer. The calculated frequencies of H¹⁴N₃, Me¹⁴N₃ and the *anti* and *gauche* conformations of Et¹⁴N₃ are included in Tables 6-9, respectively.

The scaled azide force field of VN₃ was transferred to 2-azido-1,3-butadiene [10] and to 2,3-diazido-1,3-butadiene [11] with reasonable success. We have further transferred the scaled force field of the -CH₂N₃ fragment of

TABLE 10

"Experimental" and scaled quantum mechanical force fields for the azide part of HN_3 , CH_3N_3 and $\text{CH}_3\text{CH}_2\text{N}_3$ (*anti*)

Constant ^a	HN_3				CH_3N_3		<i>Anti</i> $\text{CH}_3\text{CH}_2\text{N}_3$ DZ	Scale factor DZ
	HF	DZ	Exp. ^b	Exp. ^c	DZ	Exp. ^c		
$\text{N}\equiv\text{N}$	17.905	17.735	16.00 ^d	17.181	17.215	16.607	17.073	0.788
$\text{N}\equiv\text{N}/\text{N}=\text{N}$	-1.898	1.755	0.73	1.00 ^d	1.797	1.00 ^d	1.805	
$\text{N}\equiv\text{N}/\text{N}-\text{X}$	-0.149	-0.115			-0.129		-0.150	
$\text{N}\equiv\text{N}/\text{N}\equiv\text{N}=\text{N}$	0.072	-0.044		0.412	-0.076		-0.070	
$\text{N}\equiv\text{N}/\text{N}=\text{N}-\text{X}$	-0.015	-0.044			-0.114		-0.107	
$\text{N}=\text{N}$	8.844	8.854	9.86	8.673	9.380	8.189	9.666	1.225 ^e
$\text{N}=\text{N}/\text{N}-\text{X}$	0.051	-0.008			0.190		0.177	
$\text{N}=\text{N}/\text{N}\equiv\text{N}=\text{N}$	0.255	0.213		0.412	0.224		0.228	
$\text{N}=\text{N}/\text{N}=\text{N}-\text{X}$	0.786	0.834	0.838	0.466	0.765	0.35 ^d	0.725	
$\text{N}-\text{X}$	6.174	6.169	6.757	6.231	4.407	4.890	4.231	0.915 ^f , 0.982 ^{g,h}
$\text{N}-\text{X}/\text{N}\equiv\text{N}=\text{N}$	0.013	-0.021			-0.003		-0.017	
$\text{N}-\text{X}/\text{N}=\text{N}-\text{X}$	0.214	0.276			0.593	0.35 ^d	0.516	
$\text{N}\equiv\text{N}=\text{N}$	0.613	0.624	0.611	0.617	0.624	0.758	0.629	0.788
$\text{N}\equiv\text{N}=\text{N}/\text{N}=\text{N}-\text{X}$	0.083	0.067	0.048		0.103		0.100	
$\text{N}=\text{N}-\text{X}$	0.768	0.817	0.729	0.762	0.952	0.628	0.873	0.725 ^f , 0.696 ^{g,h}
$\tau_{\text{N}=\text{N}}$	0.0081	0.0136		0.781 ⁱ	0.0067	0.598	0.0080	0.777 ^f , 0.621 ^g , 0.687 ^h

^aUnits: mdyn Å^{-1} (stretch and stretch/stretch), mdyn rad^{-1} (stretch/bend) and mdyn Å rad^{-1} (bend and bend/bend). ^bFrom ref. 35.^cFrom ref. 46. ^dAssumed. ^eThe off-diagonal terms have been scaled by $x_{\text{N}=\text{N}} = 0.70$; see text. ^fThis scale factor applies to HN_3 .^gThis scale factor applies to CH_3N_3 . ^hThis scale factor applies to $\text{CH}_3\text{CH}_2\text{N}_3$. ⁱThe corresponding coordinate is defined as a bending of a linear chain.

the *gauche* conformation of EtN_3 to the all *gauche* series $\text{R}-\text{CH}_2\text{N}_3$ ($\text{R} = -\text{C}\equiv\text{N}$ [47], $-\text{C}\equiv\text{CH}$ [14], $-\text{C}\equiv\text{C}-\text{CH}_3$ [48] and $-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$ [49]). For all these molecules we have obtained excellent agreement with the observations.

The final interpretation of the IR and Raman spectra of EtN_3 [23], and the identification of the *gauche* and *anti* fundamentals in particular, rests mainly on the force fields developed here, but a detailed account will be given elsewhere [23]. The vibrational spectra of azidopropane have recently been recorded in this laboratory, but they have not yet been analyzed [50]. We hope that it will be possible to determine the conformational properties of this molecule from force field calculations alone combining our scaled $-\text{CH}_2\text{N}_3$ force field from EtN_3 and the standard hydrocarbon force field of Snyder and Schachtschneider [51].

For the sake of brevity, we do not give the complete harmonic force fields of MeN_3 and EtN_3 . The force fields are available from the authors upon request and will be published together with the vibrational spectra [44, 23].

Infrared intensities

The assumptions and approximations involved in calculating infrared intensities from dipole moment first derivatives, obtained numerically from permanent dipole moments in distorted structures, make the results, at best, qualitative. Minute changes in the L-matrix, i.e. in the force field, can have large effects on the calculated intensities. For the azides, the dipole moment derivatives with respect to the $\text{N}\equiv\text{N}$ and $\text{N}=\text{N}$ stretching coordinates are exceptionally large, and small differences in the scaled force fields, arising from different approximations in the scaling procedure or from different weighting of the experimental data, change the calculated, integrated intensities of some bands by up to a factor of two. Nevertheless, when working with highly unstable molecules, a qualitative prediction is far better than none at all. Since IR spectra are most commonly presented as percentage transmission, i.e. in a logarithmic scale, the theoretical predictions often appear better than expected.

The calculated intensities are included in Tables 6–9. No experimental measurements have been carried out, but, for a comparison, the experimental and theoretical IR vapour phase spectra of azidomethane [44] and azidoethane [23] are given in Figs. 6 and 7, respectively. The simulated spectra were obtained by co-adding the (properly scaled) theoretical vapour phase band contours, which were calculated assuming identical rotational constants in the upper and in the ground vibrational states [52]. In this approximation the central Q-branches of the A- and C-type bands are often calculated too sharp, as seen from Figs. 6 and 7, and possible resonances are also neglected. The theoretical spectrum of azidoethane was obtained by applying a statistical weight of two for the *gauche* conformation and assuming an energy difference of 0.6 kJ mol^{-1} between the *gauche* and the *anti* conformations

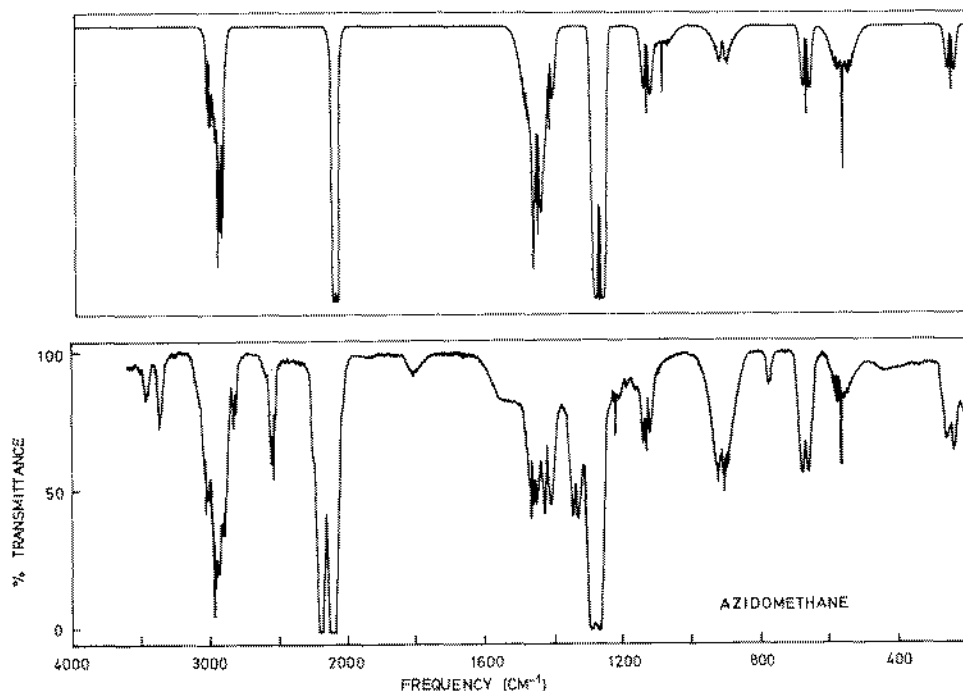


Fig. 6. The theoretical (top) and experimental (bottom) IR vapour phase spectra of azidomethane.

[23]. As seen from Figs. 6 and 7, the correspondence between observation and theory is not overwhelming, but the relative band intensities agree, reasonably, with the observations and the band types are also reproduced quite well.

For HN_3 the calculations predict all the a' -modes to be parallel bands with very weak perpendicular components in the IR in agreement with the observations [33–40]. The a'' mode, ν_6 , is predicted to be very weak and in a recent high resolution study [40] the C-type component of ν_6 was barely observed, whereas the Coriolis-induced A-type lines dominate the ν_6 band. The differences in the calculated intensities for HN_3 using the DZ or the HF basis set seem to favour the DZ basis at this level of approximation, but this may be by pure coincidence.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Jan Almlöf and Dr Trygve U. Helgaker for their interest, assistance and valuable suggestions.

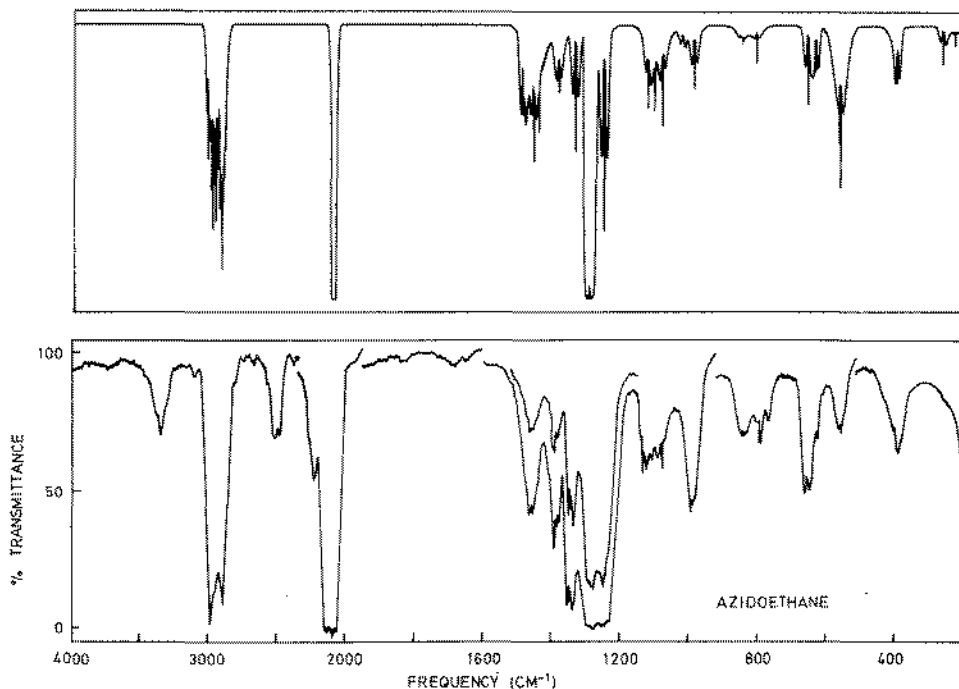


Fig. 7. The theoretical (top) and experimental (bottom) IR vapour phase spectra of azidoethane.

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