IR Spectra, Crystal Structure, Dipole Moment, *ab initio* and AM1 Study of 1,2-Dinitroethane

Yu-Lin Lam, Lip Lin Koh and Hsing Hua Huang *
Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore 0511

IR spectra of 1,2-dinitroethane in the solid, solution and vapour phases, together with Raman measurements of the compound in the solid, liquid and solution states are reported and assignment of frequencies made. Vibrational frequencies of the *gauche* and *trans* rotamers of the molecule have also been calculated at the AM1, HF/3-21G*, HF/6-31G*, MP2/3-21G* and MP2/6-31G* levels and the results are compared with the experimental frequencies.

Examination of the IR and Raman spectra suggests that the compound exists in the polar *gauche* conformation in the solid state and as a mixture of the *gauche* and *trans* rotamers in solution. The dipole moment of the compound has also been measured in benzene over a range of temperatures. Analysis of the relative permittivity data shows that at 25 °C in solution, the compound exists approximately in the ratio 92% *gauche* to 8% *trans*. The experimentally derived values of the energy difference between the *gauche* and *trans* rotamers, the dihedral angle of the *gauche* rotamer and the *gauche*/*trans* population quotient are compared with values predicted by *ab initio* methods and the semiempirical MO program AMPAC using AM1 parametrization.

The crystal and molecular structure of 1,2-dinitroethane has also been determined by single-crystal X-ray diffraction methods. The molecule crystallizes in the tetragonal space group $I4_1/a$, a = 13.305(1) Å, c = 11.121(3) Å, V = 1968.8(6) Å^3, Z = 16, Mo-Kα radiation, λ = 0.710 69 Å, μ = 0.148 mm^{-1}. The structure was refined to a R factor of 0.033. The molecule adopts a *gauche* conformation with a N–C–C–N torsion angle of 73.5(2)°. The central C–C bond of the molecule is markedly shorter than a normal C–C bond. Each NO_2 group is coplanar with the N–C–C plane containing the central carbon atoms.

Although many physical studies[1–4] of rotational isomerism in polar 1,2-disubstituted ethanes have been made, there has been no systematic study of 1,2-dinitroethane, the prototype of the vicinal dinitroethane family of compounds. We have therefore undertaken a physico-chemical study of this compound by IR and Raman spectroscopy, and dielectric and X-ray diffraction measurements. We here report the experimental results and compare observed vibrational frequencies, energy differences between *gauche* and *trans* rotamers and *gauche*/*trans* population ratios with predictions made by *ab initio* and semiempirical molecular orbital (AM1) calculations.

Experimental

Solute.—1,2-Dinitroethane was prepared by the reaction of ethene with dinitrogen tetroxide according to the method of Levy *et al.*[5] It had m.p. 39–39.5 °C (lit.,[5] 39–40 °C) (Found: C, 20.3; H, 3.35; N, 23.6. Calc. for $C_2H_4N_2O_4$: C, 20.01; H, 3.36; N, 23.33%).

Solvents.—All solvents used in the IR and Raman spectroscopic measurements were of spectroscopic grade. Benzene used in the dielectric measurements was carefully distilled and stored over sodium before use. The physical constants required in the dielectric measurements have been given previously.[6,7]

Apparatus.—Relative permittivities were determined with a heterodyne-beat meter[8] and densities and refractive indices by standard procedures.[9]

Solid-state IR spectra were recorded for Nujol and hexachlorobutadiene mulls and for KBr pressed-disc samples. Solution-state spectra were obtained using solvents such as carbon tetrachloride, carbon disulfide, benzene, chloroform and acetonitrile. The concentrations of the various solutions were expressed in terms of weight percentages. The IR absorption spectrum of the vapour at 63 °C/1 mmHg was also recorded by means of a 10 cm long gas cell with KBr windows. A Perkin-Elmer 1710 IR spectrophotometer with a spectral resolution of ± 2 cm^{-1} and wavenumber accuracy of ± 0.01 cm^{-1} was used for all these IR measurements. The IR results are given in Table 1. The numbers in parentheses after each frequency give some idea of the absorption peak heights and thus indicate the approximate relative intensities of the different bands.

Solid-, liquid- and solution-state Raman spectra were recorded using the 4880 Å line of a Spectraphysic argon-ion laser and a JESCO NR1000 spectrometer. The instrument was calibrated with argon emission lines with a spectral resolution of ± 0.15 cm^{-1}. An indication of the peak heights is given in Table 1. Raman polarization data obtained for the liquid-state are also shown.

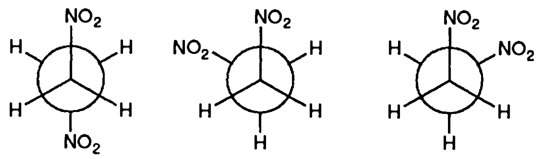
Calculations.—*Ab initio* calculations were carried out with the GAUSSIAN 86[10] or GAUSSIAN 90[11] programs using different basis sets (HF/3-21G*, HF/6-31G*, MP2/3-21G*, MP2/6-31G*). Geometries were completely optimized within the appropriate point group. All geometry opitimizations and vibrational frequency calculations were performed using analytical derivative methods. GAUSSIAN 86 programs were run on a NEC SX-1A computer and GAUSSIAN 90 on a CONVEX C3200 computer.

Semiempirical molecular orbital calculations were performed using the program[12] AMPAC 2.1 with AM1 parametrization.[13] Full geometry optimization was performed for each incremental value of the ethane C–C torsion angle. Torsion or dihedral angles were defined by the atoms N–C–C–N by the convention of Klyne and Prelog.[14] Calculations were performed on a VAX 8650 computer using Fortran 77 operating under VMS.

Table 1 Infrared and Raman spectra of 1,2-dinitroethane in the solid, liquid and solution states[a]

Infrared							Raman					
KBr	CCl_4[c] (1.3%)[b]	CH_3CN[c] (2.9%)[b]	Solid	Peak height	Liquid	Peak height	CH_3CN[c] (29.3%)[b]	Peak height	$CHCl_3$[c] (9.4%)[b]	Peak height	Class	Approximate group assignment
3029(71)	—	3033(15)	3025	17	3025	24 p(0.36)	X		X		A	ν_{CH}(asym)
2983(59)	2960(8)	X	2984	27½	2975	81 p(0.05)	X		2983	62	A	ν_{CH}(sym)
2930(48½)	2027(10)	2930(13½)	—		—		—		—			
1578(88)			1575	8	1570	14 dp	1573	16	1572	16	B	ν_{NO_2}(asym)
1548(91½)	1572(23)	1568(99½)	1550	5	—		—		—			
—	*1540(3)*	—	—		—		—		—		B_u	
1418(87)	1417(4)	X	1412	11	1410	15 p(0.53)	X		1420	12½	A	δ_{CH_2}(bend)
1393(83)	1383(3)	X	1393	91	1385	100 p(0.14)	X		1390	97	A	ν_{NO_2}(sym)
1360(84½)	1362(4)	X	1363	22	1365	20 p(0.54)	1375	58	1360	21	A	ρ_{HCH}(wag)
1330(80)	1330(1)	1332(20)	—		—		—		—			
1270(65½)	1261(12)	1260(14)	1270	18	1255	12 p(0.62)	1262	13	1260	20	A	ρ_{HCH}(twist)
1229(72)	—	1219(15)	1230	8½	1218	8 dp	1230	6½	X		B	
1098(27)	1098(11½)	1098(sh)	1095	2	1085	5 p	—		—		A	ν_{C-C}
—	*1016(12½)*	—	—		—		—		—		A_u	ρ_{HCH}(rock)
993(58½)	—	997(9)	992	20	990	32 p(0.09)	998	29	995	31	A	
967(66½)	—	970(9½)	967	8	970	7½ dp	970	sh	972	8	B	
—	—	—	—		*935*	*4 p*	—		*940*	*8*	A_g	ν_{CN}
881(71)	—	880(25)	—		—		—		—			
871(78)	871(3½)	872(26)	870	62	870	100 p(0.05)	873	96½	872	100	A	
680(40)	—	—										δ_{NO_2}(bend)
656(67½)	663(1)	665(12)	655	12	665	68 p(0.03)	665	12	X		A	
608(78)	618(1)	615(18)	615	10½	610	8 dp	620	10	X		B	ρ_{NO_2}(wag)
592(sh)	590(½)	—	595	sh	595	sh	—		—			
562(65½)	560(2)	559(12½)	565	5½	560	7 p(0.5)	560	8	568	9½	A	
547(65½)	—	—	—		—		—		—			ρ_{NO_2}(rock)
481(30)	X	483(8)	—		—		—		—			
413(41)	—	420(12)	415	28	420	15 p(0.38)	423	24	425	31	A	
			310	7½	310	5 dp	320	10	X		B	δ_{C-C-NO_2}
			285	8½	260	35½ p(?)	270	12	X			

[a] Relative intensities of bands are indicated by percentage absorption given in parentheses after the wavenumbers. Numbers in underlined italics denote an additional band in solution attributable to the *trans*-form. X indicates masking by solvent while — indicates absence of absorption. dp denotes a depolarized and p a polarized band. [b] Weight percentage. [c] ε_{20} (relative permittivity of the solvent at 20 °C) = 2.238 (CCl_4), 37.5 (CH_3CN), 4.806 ($CHCl_3$).



1, *trans* **2**, *gauche* **3**, *gauche*

Fig. 1 Stable conformations of 1,2-dinitroethane

Crystal Structure Determination and Refinement.—Crystals of 1,2-dinitroethane were obtained from solution in dichloromethane–hexane at 7 °C. A single crystal was wedged and sealed in a quartz capillary for data collection at room temperature using a Siemens R3m/V200 diffractometer with Mo-Kα radiation (λ = 0.710 69 Å). Crystal data: $C_2H_4N_2O_4$, M = 120.1, tetragonal (space group $I4_1/a$); a = 13.305(1) Å, c = 11.121(3) Å; V = 1968.8(6) Å^3 d_{calc} = 1.620 g cm^{-3}. Z = 16. A total of 859 independent reflections were recorded with $3° < 2\theta < 50°$ of which 693 with $I > 2.0(I)$ were considered unique and observed. Cell constants were determined by least-squares fit to the setting parameters of 15 reflections. Intensity data were collected by Wyckoff scan. Lorentz and polarization corrections, structure solution by direct methods, full-matrix least-squares refinements and preparation of figures were all performed by the programs of SHELXTL-Plus.[15] Non-hydrogen atoms were refined anisotropically. Atomic co-ordinates of hydrogen atoms were also refined with fixed isotropic thermal parameters. R and R_w factors after refinement of 86 parameters were 0.033 and 0.042 respectively. The largest peak in the final Fourier difference map was 0.25 e Å^{-3}. Tables of atomic co-ordinates, bond length and angles, thermal parameters and torsion angles have been deposited at the Cambridge Crystallographic Data Centre.*

Spectroscopy.—The vibrational spectroscopy results for the solid, liquid and solution states are given in Table 1. The IR spectral data for the vapour phase are given in a supplementary table. In Table 1, the following frequencies, observed in a KBr disc, possibly due to combination or overtone bands have been omitted for convenience of presentation as only very weak and ill-resolved bands were observed in solution in this range: 2808(31), 2757(31½), 2684(31½), 2620(29), 2586(33½), 2540(30½), 2414(33½), 2359(35), 2330(34), 2280(33½) cm^{-1}).

Fig. 1 shows the Newman projections of the likely rotamers of the compound, the *trans* and *gauche* conformations.

Fundamental Vibrational Modes for the Rotational Isomers.—Table 2 summarizes the vibrational species of the compound. Theory requires the centrosymmetric *trans* form (point group C_{2h}) to have fifteen infra-red (A_u and B_u) and fifteen Raman active fundamentals (A_g and B_g). However because this compound exists exclusively in the *gauche* conformation in the solid, as shown by our X-ray results, and in very low *trans* concentration in solution, as shown by our dipole moment results (*vide infra*), we should expect to see no *trans* bands in the solid and very few, if any, of these bands in solution. The *gauche* rotamer has only a C_2 axis of symmetry and thus belongs to the C_2 point group. Accordingly it would have sixteen

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* For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Table 2 Vibrational species of 1,2-dinitroethane

Point group	Vibrational species	Activity IR	Activity Raman	Total number of fundamentals
C_{2h}	A_g	ia	p	10
	A_u	a	x	6
	B_g	ia	dp	5
	B_u	a	x	9
C_2	A	a	p	16
	B	a	dp	14

[a] ia = inactive; a = active; p = polarized; dp = depolarized; x = forbidden.

fundamentals associated with class A and fourteen with class B. The A and B types are both IR-active and give rise to Raman polarized and Raman depolarized lines respectively.

Comparison of the IR and Raman spectra of the compound in the solid state shows that many absorption bands coincide in frequency. This is evidence for the absence of a centre of symmetry in the conformation of the molecule in the solid state and consequently its likely structure is *gauche*. However the presence of two extra IR bands at 1540 and 1016 cm^{-1} and an extra Raman band at 940 cm^{-1} of the solution-state spectra suggests strongly that both *trans* and *gauche* rotamers are present in solution. The bands at 1540 and 1016 cm^{-1} practically disappear in acetonitrile but reappear in solvents of low relative permittivity like carbon tetrachloride and carbon disulfide. This suggests that these extra absorptions are likely to be the *trans* bands. Hence it follows that the polar rotamer **2** or **3** where the nitro groups are *gauche* to each other is the preferred form in the solid state. This is consistent with most of the vicinal dinitro compounds studied so far.[16–19]

The extra bands observed in solution are also significant in so far as they can be associated with the skeletal frequencies of the *trans* form. A *trans* rotamer, as Table 2 shows, would also be expected to have 15 IR-active fundamentals due to the A_u and B_u modes. However many of these frequencies are likely to overlap with those of the *gauche* form, and thus the extra frequencies observed in solution in either the IR or Raman spectra are just the strongest ones of the *trans* rotamer. The extra band at 1016 cm^{-1}, for instance, which is observed only in the IR spectrum of the carbon tetrachloride solution could be assigned to the trans A_u mode of the CH_2 rocking vibration, a mode which is IR-active but Raman-forbidden. Similarly, the IR band at 1540 cm^{-1} in carbon tetrachloride which could be the *trans* equivalent of the *gauche* fundamental at 1572 cm^{-1}, is assigned to the *trans* B_u mode of the asymmetric stretching of the NO_2 group. The extra band at *ca.* 940 cm^{-1} in the Raman spectra of the liquid-state and chloroform solution, which is polarized and has no observed counterpart in the IR spectra, may be attributed to the *trans* A_g mode of the C–N stretching vibration, a mode which is inactive in the IR.

In making group vibrational assignments as shown in Table 1, we have kept in mind the assignments made for nitromethane[20] and the normal co-ordinate calculations previously carried out on 1,2-dicyanoethane[21] and nitroethane.[22] Comparing the spectra of 1,2-dinitroethane to those of 1,2-dicyanoethane, extra bands are found at 881 and 871 cm^{-1} in the IR spectra and 873 cm^{-1} in the Raman spectra. These bands are assigned to the C–N stretching vibration in C–NO_2 since they do not appear in the spectrum of the cyano analogue of this compound where the C–NO_2 vibrations do not exist. Furthermore, it was observed that the band at 870 cm^{-1} in the Raman spectrum is polarized. This frequency may thus be assigned to the A class of the C–N stretching mode (Table 1). Similarly, we can also assign the A and B classes on the basis of polarization data to other frequencies in the molecule.

The NO_2 stretching modes are known to give rise to strong absorption in the 1560–1340 cm^{-1} region.[23] This has also been found to be the case here. The strong IR band at 1578 cm^{-1}, to which there corresponds a depolarized Raman line at 1570 cm^{-1}, is interpreted to be the B fundamental of the asymmetric NO_2 stretching of the *gauche* rotamer while the polarized Raman line at 1385 cm^{-1} with a strong IR counterpart at 1393 cm^{-1} is assigned to the A class of the symmetric NO_2 stretching. In addition, the frequencies in the 680–560 cm^{-1} region have been assigned to the bending and wagging modes of the NO_2 groups. The polarized Raman line at 665 cm^{-1} has a corresponding line at 656 cm^{-1} in the IR spectra and is thus assigned to the A fundamental of the NO_2 bending mode while the IR bands at 608 and 562 cm^{-1}, to which there correspond a broad, depolarized Raman band at 610 cm^{-1} and a polarized Raman line at 560 cm^{-1}, are attributed to the B and A classes of the NO_2 wagging mode.

The bands associated with the C–C stretching and CH_2 deformation modes are expected in the spectral region 1420–960 cm^{-1}. However, not all the fundamentals associated with these vibrations are observed.

Dipole Moment Measurements.—Results of the dielectric measurements in benzene at various temperatures are summarized in Table 3. The large dipole moment means that the polar rotamer **2** or **3** must be present in high proportion in this solvent. From Table 3, it can also be seen that the dipole moment of the compound decreases with increasing temperature in benzene, indicating that the *gauche* rotamer is more stable than the *trans*, and is higher in population in this solvent.

The dipole moment (μ_g) of the *gauche* rotamer of a molecule YCR_2-CR_2Y can be calculated from eqn. (1), where μ_0 is the

$$\mu_g = \mu(2\theta) = 2\mu_0 \sin\alpha \cos\theta \qquad (1)$$

moment of the symmetrical half of the molecule (CR_2Y), α is the supplement of the central C–C–Y bond angle and 2θ is the dihedral angle between the two C–C–Y planes.[24] In our calculations on 1,2-dinitroethane, μ_0 was taken to be the value of the dipole moment of nitromethane (10.45×10^{-30} cm)[25] with its direction along the C–NO_2 bond while the values of α (66.9°) and 2θ (73.5°) were taken from the results of our X-ray diffraction study of the molecule. Substitution of these values into eqn. (1) gives a dipole moment (μ_g) of 15.48×10^{-30} cm for the *gauche* rotamer. We have also calculated μ_g by semiempirical and *ab initio* methods with the following results: 19.38, 18.80, 19.82, 15.08 and 16.38 $\times 10^{-30}$ cm by AM1, HF/3-21G*, HF/6-31G*, MP2/3-21G* and MP2/6-31G* respectively. The dipole moment for each level was calculated from the corresponding geometry at that level.

An estimate[26] of the *gauche*-rotamer population (x%) in solution can be made from eqn. (2), which on substituting the

$$x = \frac{100\mu^2_{\text{obs}}}{\mu^2_g} \qquad (2)$$

observed moment and a μ_g value of 15.48×10^{-30} cm, yields a population of 92% *gauche* and 8% *trans*. The very high proportion of the *gauche* rotamer suggests that in this compound the *gauche* conformation is inherently much more stable than the *trans*. This stability appears to be another manifestation of the '*gauche* effect' noted by Wolfe;[27] it is consistent with the theory that there is a tendency for a structure which has the maximum number of *gauche* interactions between the adjacent electron pairs and/or polar bonds to be favoured. In 1,2-dinitroethane, each nitro group has a very high polarity and possesses two electron pairs on each oxygen atom and one

Table 3 Molar polarization, refractions and dipole moments at infinite dilution of 1,2-dinitroethane. Incremental changes in the relative permittivities, densities and refractive indices ($\Delta\varepsilon$, Δd, and Δn) were measured for solutions having solute weight fractions w_2. The coefficients α, β and γ were derived from the relations $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$, $\beta d_1 = \Sigma\Delta d/\Sigma w_2$ and $\gamma n_1^2 = \Sigma\Delta n^2/\Sigma w_2$.

T/°C	Solvent	Conc. range ($10^5 w_2$)	$\alpha\varepsilon_1$	β	γ	P_2/cm^3	R_D/cm^3	μ^a/ 10^{-30} cm
7	Benzene	300–650	20.36	0.399		466.69		15.05 ± 0.08
25	Benzene	300–700	17.82	0.349	−0.085	428.89	21.8	14.85 ± 0.15
45	Benzene	350–650	15.97	0.436		399.52		14.77 ± 0.05

[a] $P_D = 1.05\ R_D$; R_D(calc) = 22.7.

Table 4 Total energies (Hartrees) and differences (kJ mol^{-1}) associated with the *gauche* and *trans* rotamers in 1,2-dinitroethane

Method	*gauche*	*trans*	ΔE^a	Gauche population (%)
AM1	−47.959 0^b	−41.422 9^b	−6.54	96
HF/3-21G*	−483.360 34	−483.360 54	0.52	62
HF/6.31G*	−486.164 37	−486.163 25	−2.92	87
MP2/3-21G*	−484.362 27	−484.361 74	−1.40	78
MP2/6-31G*	−487.532 16	−487.529 06	−8.12	98

[a] $\Delta E = E_g - E_t$ (kJ mol^{-1}). [b] $\Delta H_f°$/kJ mol^{-1}.

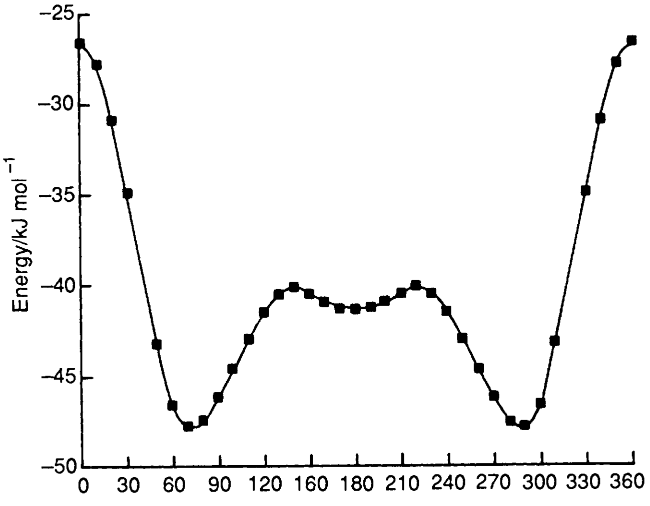

Fig. 2 Energy *versus* torsion angle diagram of 1,2-dinitroethane

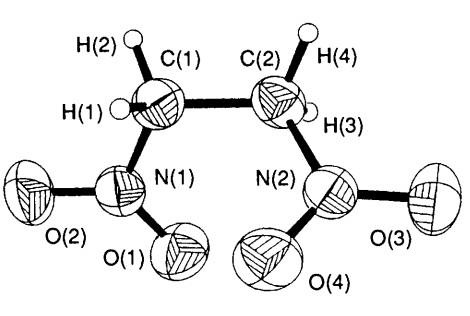

Fig. 3 Thermal ellipsoid diagram of 1,2-dinitroethane

electron pair on the nitrogen atom. However the final conformation adopted is still dependent on the overall balance of the attraction and repulsion between the groups in the molecule.

The internal energy difference between the rotational isomers, $\Delta E = E_g - E_t$, of the molecule was calculated[26] to be −4.33 kJ mol^{-1}.

The variation of the heat of formation with the dihedral angle (2θ) obtained from AMPAC calculations with AM1 parametrization and full geometry optimization is shown in Fig. 2. Clearly the *gauche* rotamer has a lower energy than the *trans* form, differing from it by 6.35 kJ mol^{-1}. The torsion angle of the *gauche* rotamer with the lowest energy was found to be 70° and the Boltzmann distribution to be 96% *gauche* and 4% *trans*. These results compare well with those determined experimentally.

The results of the AM1 and *ab initio* calculations of the energies of the *gauche* and *trans* rotamers of 1,2-dinitroethane are presented in Table 4. Clearly there is qualitative agreement between experiment and the MP2/6-31G*, MP2/3-21G* and HF/6-31G* levels of theory, the quantitative agreement being best for AM1 and MP2/6-31G*. However, the HF/3-21G* level of calculation fails to reproduce the observed order of stability predicting the *trans* rotamer to be slightly more stable than the *gauche*.

The use of the more flexible 6-31G* basis set gave larger absolute values of ΔE than those obtained at the 3-21G* level. The inclusion of electron correlation through the MP2 approximation further increases this value. Thus at the 6-31G* level, the MP2 and HF ΔE values were found to be −8.122 and −2.924 kJ mol^{-1} respectively. From the Boltzmann equation, this corresponds to a *gauche* population of 98% and 87% respectively. On the other hand, the MP2 and HF calculations based on the 3-21G* basis set produced ΔE values of −1.401 and 0.524 kJ mol^{-1} corresponding to *gauche* populations of 78% and 62% respectively. These latter values compare less satisfactorily with the experimental result of 92% *gauche*. Nevertheless the overall results of the calculations indicate that the inclusion of polarization functions also stabilizes the *gauche* form and hence increases the energy difference between the two rotamers.

X-Ray Structure Determination.—Crystal structure of 1,2-*dinitroethane*. Each asymmetric unit of the cell contains one molecule in a general position. The inherent two-fold symmetry of the molecule was not utilized in the packing. Although the molecule does not have crystallographic symmetry, it shows approximate two-fold rotational symmetry. Fig. 3 depicts the structure and defines the atomic numbering of the molecule.

After least-squares refinements, the molecule showed a remarkably short central C–C bond length of 1.488(3) Å which is significantly shorter than the standard tetrahedral C–C bond length of 1.544 Å or the reported value of 1.561(6) Å in 1,2-dicyanoethane.[28] This shortening appears to be the result of the electron-withdrawing effect of the NO_2 groups which facilitates the partial delocalization of the electrons of the C–H bonds and their transference to the carbon chain through chain-hyperconjugation.[29] Another plausible reason may be the modification of the s/p hybridization ratio by the electronic interaction of the NO_2-groups so as to increase the s character of the C–C bond at the expense of the C–H bond.[30]

The molecule as a whole adopts a *gauche* conformation with a N(1)–C(1)–C(2)–N(2) torsion angle of −73.5(2)°. The resulting structure shows that the two NO_2 groups are planar. They are also in nearly coplanar conformation with respect to the central C–C bond, the torsion angles O(4)–N(2)–C(2)–C(1) and O(1)–N(1)–C(1)–C(2) being −4.1(2)° and 4.6(3)° respectively. In this conformation, the O(1) ••• O(4) contact distance between the NO_2-groups is 3.043 Å. This value is slightly larger than the O ••• O interatomic distance between the overlapping oxygens in 1,1′-dinitrobicyclopropyl (2.95 Å)[31] and is accompanied by a larger N–C–C–N torsion angle in 1,2-dinitroethane. In addition the difference between the O(1)–N(1)–C(1) and O(4)–N(2)–C(2) bond angles [119.8(2)° and 119.9(3)°] on one hand and the O–N–C bond angles involving the non-overlapping oxygens [116.7(2)° and 116.9(2)°] on the other, suggests the presence of repulsive oxygens. However the observed structure shows that in the absence of steric hindrance, the conformation with both NO_2 groups coplanar with the central carbons is inherently more stable than a conformation such as that observed in 2,3-dimethyl-2,3-dinitrobutane[31] where the NO_2 groups are perpendicular to the central C–C bond. This preference of the NO_2 π-acceptor substituents for the coplanar conformation appears to be a consequence of the tendency for the HOMO of the ethane fragment to overlap effectively with the LUMO of the π-acceptor substituent[32] to reduce its energy.

The packing diagram shows that the molecules lie in layers parallel to the (110) plane. There are no unusually short intramolecular non-bonding distances.

Geometry and Vibration Frequency Calculations.—The optimized geometries of the *gauche* and *trans* rotamers of 1,2-dinitroethane obtained by *ab initio* and semiempirical AM1 calculations show each NO_2-group to be coplanar with the central C–C bond in agreement with the results obtained from our X-ray diffraction study.†

All levels of theory predict a C–C bond which is significantly shorter than the calculated value of 1.527–1.542 Å in the ethane molecule.[33] This appears to be an additional consequence of the two factors mentioned earlier: (*a*) the electron-withdrawing effect of the NO_2 group causing the HOMO of the ethane fragment in the molecule to interact with the LUMO of the nitrogen atoms, and (*b*) the chain-hyperconjugation effect.

From MP2/6-31G* and HF/6-31G* calculations, the NCCN torsion angle of the *gauche* form was found to be 65° and 69.5° respectively, a decrease of 4–8° from the experimental result of 73.5°. However, the values obtained at the MP2/3-21G* and HF/3-21G* levels were 73.5° and 75.6°, in better agreement with our X-ray result. Semiempirical AM1 calculations predict a NCCN torsion angle of 71.5° which also compares well with experiment.

Comparing mode for mode, the frequencies of the *gauche* and *trans* rotamers computed at the same level of theory are found to have an average difference of 36 cm^{-1}. The smallest difference between the frequencies (31 cm^{-1}) is found at the 6-31G* level, which also shows the smallest difference in bond lengths and angles between the *gauche* and *trans* rotamers, while the largest difference between the frequencies is at the 3-21G* level which also shows the largest difference in geometry between the two conformers. Moreover, the vibrational modes involving the NO_2-groups tend to shift to higher frequencies in going from the 3-21G* to 6-31G* level. This result parallels the bond shortening that is observed when polarization functions are included in the calculations.

Scaling the MP2/3-21G* and MP2/6-31G* frequencies downwards by 7.0 and 6.5% respectively, and the HF/3-21G* and HF/6-31G* frequencies by 10% brings them into fairly good agreement with experiment, except for the NO_2 stretches. The mean absolute deviations of the HF/3-21G*, HF/6-31G*, MP2/3-21G* and MP2/6-31G* frequencies from experimental results are 64, 46, 67 and 36 cm^{-1} respectively (51, 27, 47 and 25 cm^{-1} when the NO_2 stretches are omitted). Thus these values indicate that the 6-31G* frequencies of the *gauche* rotamer of 1,2-dinitroethane are in general closer to the experimental data than those at the 3-21G* level.

At the 6-31G* level, the predicted asymmetric NO_2 stretch of the *gauche* rotamer of 1,2-dinitroethane is too high by *ca.* 144 cm^{-1}. This over-estimation has also been previously observed in the results of a similar calculation on nitromethane[20] and has been attributed to the neglect of a low-lying configuration which contains two electrons in an N–O antibonding orbital.

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† Tables of calculated and observed geometric parameters and fundamental vibrational frequencies are available as Supplementary Material (Supp. Pub. No. 56916, 6 pages).

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