CHAPTER 16

THEORETICAL AND EXPERIMENTAL MODELS OF MOLECULES ILLUSTRATED WITH QUANTUM-CHEMICAL CALCULATIONS OF ELECTRONIC STRUCTURE OF H_2CN_2 ISOMERS

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Abstract: To compare aspects of theoretical and experimental models of molecules, we employ the results of quantum-chemical calculations on diazomethane and six structural isomers with formula H_2CN_2; significant deficiencies of both models impede comparison between a calculated value of a property and a corresponding value deduced from experiment

INTRODUCTION

When, about year 1957, Coulson was reputed to have remarked to the effect that "the objective of quantum chemistry is to paint a picture, not to take a photograph", conditions regarding both theoretical methods and the practice of calculation were much more primitive than those at present. During the past half century, quantum-chemical computations – as an application of quantum-mechanical principles and procedures for the calculation of molecular electronic structure – have evolved from being a tedious manual task, on which only a few expert and mathematically minded chemists would embark, to become a routine computation for which several computer programs, some even free of cost, are available; operation of these programs requires little understanding of either details of the models or algorithms or even the nature of the calculations in relation to their prospectively fundamental quantum-mechanical underpinning. Not only do the innumerable publications accumulated in this field include many examples in which their authors have focused on artefacts of quantum-mechanical methods, such as wave functions in wave mechanics or their purported constituent orbital components, but also terms that originated in a questionable mathematical basis have pervaded general chemical usage in a

J.C.A. Boeyens and J.F. Ogilvie (eds.), Models, Mysteries and Magic of Molecules, pp. 341–364.

purely qualitative and loose manner devoid of mathematical significance, such as the description of a tetrahedrally ‘ligated’ carbon atom as being of type “sp^3”. The practice of quantum chemistry is almost invariably built on a model of atomic orbitals and their combinations that serve as a basis of calculations of electronic structure with atomic nuclei at chosen positions, but commonly the latter relative positions are varied for the purpose of finding a minimum energy of the ensemble of electronic and nuclear particles. As we demonstrate here, this model proves practical for the purpose of estimating molecular properties that might be compared with deductions from experiment, even though such a comparison be imperfect, as we discuss here also. In the present work we hence undertake not merely to calculate some properties of selected molecular species for actual or prospective comparison with apparently related experimental data but also to appraise the scene of those calculations so as to illuminate both the underlying models and possible pitfalls in such comparisons.

For this purpose we have selected molecular species in a set specified according to a chemical formula H_2CN_2; this merely pentatomic molecular entity comprising atomic centres of three types is remarkable in implying a possible existence of multiple chemical compounds, some already characterized and others prospective, even if likely unstable. All species result from structural isomerism – a varied topology or order of putative connectivity of relative spatial locations of atomic centres. Among thirteen such plausible isomers, those with both a nearly collinear, arrangement of massive atoms and a dihydrogenic moiety are diazomethane H_2CNN, cyanamide H_2NCN, and isocyanamide or N-aminoisonitrile H_2NNC; with hydrogenic atomic centres farther separated, carbodiimide HNCNH and nitrilimine HCNNH are characterized to some extent, but further possibilities CN(H)NH, NC(H)NH, HCN(H)N and HCN(H)N, each bearing a hydrogenic atomic centre attached at the middle member of the skeleton, are unknown experimentally. Isomers with a cyclic skeleton include diazirine or 1,1-diazirine *c*-H_2CN_2 that is stable and well characterised, and 1,2-diazirine or isodiazirine *c*-HCN(H)N not yet identified from experiment, apart from *c*-$C(NH)_2$ and *c*-$CNNH_2$ that are unknown and likely to be even less stable under conventional conditions in a laboratory. The geometric structures of the seven isomers upon which we have undertaken calculations are depicted in Figure 16-1.

The diversity of these isomers and the significant variability of the chemical properties and reactivity of the corresponding chemical substances have attracted much attention from the point of view of calculations of molecular structure. Prompted by a qualitative consideration of the interconversion of isomers [1], Hart [2] embarked on a major comparison of geometric structures through innovative calculations on five acyclic isomers; to explore the bonding and reactivity of these isomers, he employed for this purpose a basis set of gaussian lobes, and calculated molecular orbitals in a self-consistent field that were transformed to canonical localised molecular orbitals. Apart from routine calculations on an individual or a few isomers, Moffat [3], Thomson and Glidewell [4], Guimon et al. [5], Boldyrev et al. [6], Kawauchi et al. [7] and Maier et al. [8] performed increasingly sophisticated calculations on multiple isomers.Although Hart [2], for lack of automatic optimization

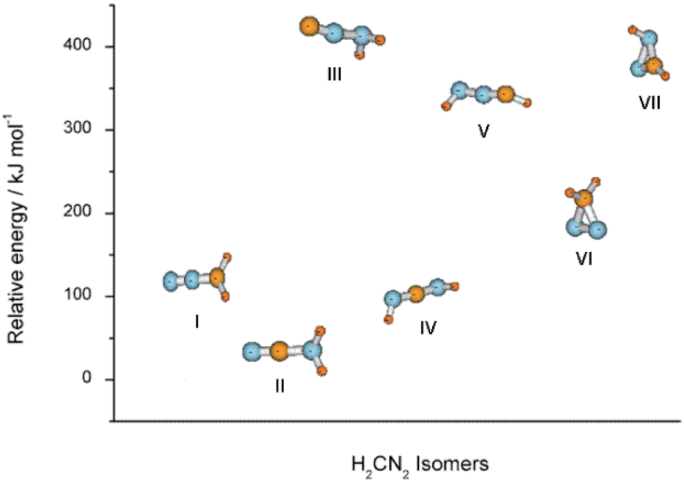

Figure 16-1. Depiction of geometric structures of isomers of H_2CN_2 showing the relations between those structures and the relative energies according to data in Table 16-1; the molecules are diazomethane I, cyanamide II, isocyanamide III, carbodiimide IV, nitrilimine V, 1,1-diazirine VI and 1,2-diazirine VII

of geometric structural parameters, applied a manual method for this purpose, subsequent authors reported their estimates of optimized bond lengths and interbond angles of various isomers.

Several calculations of geometric structure of these isomers have thus been reported, but there has been little effort devoted to estimate the electric and magnetic properties and to their comparison. For instance, the vibrational polarizability describes the polarization of a molecule due to a displacement of the atomic centres from their relative equilibrium positions [9]; this quantity, which is represented with a tensor of second order having up to six independent components of which some might be zero by symmetry, governs the intensity in the vibrational Raman spectrum. As the value of this polarizability depends on the frequency of light that serves to excite the Raman scattering, a calculation for comparison with experiment might take this factor into consideration. Such vibrational polarizability causes a net contribution to the total molar polarization that is smaller than the electronic polarizability with all atomic nuclei in their equilibrium positions, but the ratio of magnitudes of these polarizabilities varies with the nature of the molecular structure. We have calculated these quantities that are difficult to measure, particularly with chemical compounds as inconvenient to handle as diazomethane and most isomers. Whereas the electric dipolar moment is commonly deduced from splitting of lines in pure rotational transitions with a Stark effect involving an externally applied electric field, estimates of the rotational *g* factor and the magnetizability result from application of a Zeeman effect through a magnetic field on similar transitions. Although only an anisotropic component of magnetizability is experimentally evaluated in this way, it is convenient to compute the isotropic magnetizability and even the diamagnetic and paramagnetic contributions thereto that arise through the use of *London atomic orbitals* in the calculation [10]. For polyatomic molecules, the rotational *g* factor is represented by a tensor of second rank with generally six independent components. These properties are difficult to measure through a direct experiment, but their calculation presents no particular difficulty when each property is related to some aspect of the distribution of atomic nuclei and their associated electronic density.

The progressive improvement of both computer hardware and software during these five decades during which calculation of these molecular properties has become feasible has enabled much improved estimates of not only structural parameters but also other properties that might be experimentally measured directly or deduced from spectral or other experiments. As an example of the present capability of calculations of molecular electronic structure, in the present work we have conducted calculations of various electric and magnetic properties of H_2CN_2 in seven structural isomers with a basis set at a uniformly high level, for comparison with existing experimental data or for prediction for subsequent experiments; because these electric and magnetic properties can depend sensitively on molecular geometries, we specify also those geometries, and related spectral data. We interpret all these results in the light of our present understanding of the nature of the models underlying both calculations and experimental measurements.

CALCULATIONS

For all calculations of molecular electronic structure we utilized software Dalton 2.0 [11] to implement numerical solution of Schrödinger's equation and to estimate molecular properties. The electronic energy and properties we calculated with wave functions according to a basis set, denoted *aug-cc-pVTZ*, devised by Dunning and coworkers [12], involving a self-consistent field of the type complete active space and multiple configurations. The number of electrons in active shells associated with functions for one electron in a selected set varied with the particular isomer; these numbers of electrons in active shells and numbers of active orbitals, respectively, for each isomer follow: diazomethane, 4, 6; cyanamide, 10, 10; isocyanamide, 4, 6; carbodiimide, 12, 10; nitrileimine, 8, 9; 1,1-diazirine, 6, 10; 1,2-diazirine, 10, 9. The same contractions, denoted (6s3p2d|4s3p2d) for H and (11s6p3d2f|5s4p3d2f) for C and N, were employed in all calculations, in total 224 primitive and 184 contracted gaussian basis functions.

Such a basis set combines well with coupled-cluster wave functions to tend to converge in a consistent and predictable manner towards limits of the basis set and the theory. Calculation of the rotational *g* tensor and magnetizability involved use of rotational London orbitals [10]. Optimization, first order in derivatives of energy with respect to internuclear distances, yielded all reported geometric structures of arrangements of atomic centres; we calculated all reported molecular properties at these optimized geometries.

RESULTS

In several tables we present the results from our calculations. One large table contains values of parameters describing electric and magnetic properties and moments of inertia and rotational parameters of optimized structures for which such comparison is convenient. Succeeding tables contain parameters for optimized geometric structures, their vibrational wavenumbers and intensities, with experimental data for comparison if available; because the most pertinent structural parameters vary according to a particular isomer, and because the symmetries of the isomers involve four distinct point groups – C_{2v}, C_2, C_s and C_1, each with its fundamental vibrational modes in separate classes, we present one such table for each individual structural isomer, except combining content for cyanamide and isocyanamide into one table.

In each case the results are applicable to a net electrically neutral molecular species of formula $^1H_2{}^{12}C^{14}N_2$ with unit spin multiplicity and for the electronic ground state. Because our calculation pertains formally to a single molecule with coordinate axes fixed in the molecular frame oriented according to the inertial axes, we express our results generally in terms of molecular quantities and with SI units but unified atomic mass unit; to facilitate comparison with results reported elsewhere, in a few cases we present additional data converted with appropriate factors.

In an order emphasizing the structural relations, Figure 16-1 depicts the optimized geometric structures of seven isomers with chemical formula H_2CN_2 – diazomethane I, cyanamide II, isocyanamide or N-aminoisonitrile III, carbodiimide IV, nitrilimine V, diazirine VI and 1,2-diazirine VII. With one column for each isomer in the same order, Table 16-1 presents the results of calculations of electric and magnetic and some spectral properties of isolated molecules in their optimized structures that are directly comparable in this way. The first row contains the total energy of the molecular system, including relativistic corrections of types mass velocity and Darwin; the second and third rows indicate the energy of each isomer relative to that of the most stable isomer, cyanamide, per molecule and per mole respectively, appropriately rounded.

Of rows in the next group for electric properties, the fourth shows the total electric dipolar moment. The next five rows present an analysis of net electronic populations associated with each atomic centre, according to an atomic polar tensor [13]; each value listed represents the net alteration of electronic population associated with a particular atomic centre through its participation as a constituent of the particular molecule in a specific isomeric form. To distinguish the two hydrogenic atomic centres if they lie in chemically inequivalent positions, H_a is nearer a carbon atom than H_b; likewise if the two nitrogens have inequivalent positions N_a is nearer a carbon atom than N_b. The next six rows present elements of a symmetric

Table 16-1. Energies, electric dipolar moments, net atomic populations, vibrational polarizabilities and mean vibrational molecular polarization, magnetizability and contributions thereto, isotropic g tensor and nuclear and electronic paramagnetic and diamagnetic contributions thereto, principal moments of inertia and rotational parameters calculated for ${}^1H_2{}^{12}C{}^{14}N_2$ in seven structural isomers

property	diazomethane	cyanamide	isocyanamide	carbodiimide	nitrilimine	1,1-diazirine	1,2-diazirine
total energy/hartree + 148	−0.1584322	−0.2010834	−0.0508985	−0.1741517	−0.0716112	−0.1382128	−0.0694224
relative energy/10^{-18} J	18.6	0	65.5	11.7	56.4	27.4	57.4
relative energy/kJ mol^{-1}, including residual energy	104	0	394	67	333	164	340
electric dipolar moment $p/10^{-30}$ C m	5.654	13.637	14.061	7.346	7.425	5.791	9.884
atomic population on C	−0.413	0.333	0.011	0.925	−0.600	0.129	0.261
atomic population on H_a	0.118	0.195	0.198	0.321	0.244	0.017	0.103
atomic population on H_b	0.118	0.195	0.198	0.321	0.192	0.017	0.125
atomic population on N_a	0.773	−0.408	−0.127	−0.784	0.641	−0.082	−0.255
atomic population on N_b	−0.596	−0.315	−0.280	−0.784	−0.576	−0.082	−0.234
vibrational polarizability $\alpha_{aa}/10^{-41} C^2 m^2 J^{-1}$	3.432	4.956	1.491	23.876	...	0.293	1.793
vibrational polarizability $\alpha_{ab}/10^{-41} C^2 m^2 J^{-1}$	0	0	0	0	...	0	-0.031
vibrational polarizability $\alpha_{ac}/10^{-41} C^2 m^2 J^{-1}$	0	3.480	−1.477	−1.755	...	0	-0.026
vibrational polarizability $\alpha_{bb}/10^{-41} C^2 m^2 J^{-1}$	0.145	0.316	6.242	2.958	...	0.958	1.559
vibrational polarizability $\alpha_{bc}/10^{-41} C^2 m^2 J^{-1}$	0	0	0	0	...	0	0.256
vibrational polarizability $\alpha_{cc}/10^{-41} C^2 m^2 J^{-1}$	21.035	4.060	2.505	0.204	...	0.094	0.511
mean vibrational molecular polarization/10^{-30} m^3	5.673	2.151	2.360	6.232	...	0.310	0.890
magnetizability, isotropic/10^{-29} J T^{-2}	−36.55	−45.91	−43.27	−46.82	−39.39	−31.77	−37.34
magnetizability, diamagnetic/10^{-29} J T^{-2}	−180.71	−188.42	−179.00	−183.71	−178.45	−140.13	−146.49
magnetizability, paramagnetic/10^{-29} J T^{-2}	144.16	142.51	135.73	136.89	139.06	108.36	109.15
isotropic g tensor	−0.3195	0.1561	0.1445	0.0484	−0.2184	−0.1821	−0.1115
nuclear contribution to g	0.7179	0.7031	0.6922	0.6933	0.6875	0.5932	0.5952
diamagnetic contribution to g	−0.0401	−0.0401	−0.0461	−0.0414	−0.0456	−0.0576	−0.0577
paramagnetic contribution to g	−0.9973	−0.5069	−0.5016	−0.6035	−0.8603	−0.7177	−0.6490
inertial parameter $I_a/10^{-20}$ u m^2	1.807222	1.701204	1.759552	1.386995	1.421473	12.387741	12.202547
inertial parameter $I_b/10^{-20}$ u m^2	45.216582	50.258732	46.189584	49.003341	45.955446	21.381566	23.954082
inertial parameter $I_c/10^{-20}$ u m^2	47.023803	51.332726	47.110536	49.277031	46.217609	30.32326	34.43216
rotational parameter A/m^{-1}	932.7925	990.9233	958.0635	1215.4068	1185.9267	136.0832	138.1484
rotational parameter B/m^{-1}	37.2820	33.5417	36.9466	34.4010	36.6825	78.8419	70.3748
rotational parameter C/m^{-1}	35.8491	32.8399	35.7831	34.2099	36.4745	55.6931	48.959

tensor for vibrational electric dipolar polarizabilities [9] relative to principal inertial axes; for these calculations we assumed a static polarizability corresponding to zero frequency. The following row indicates the corresponding mean vibrational contribution to the total molecular electric dipolar polarization.

The next seven rows pertain to magnetic properties of each isomer in its optimized structure. The molecular magnetizability is the factor of proportionality that yields the magnetic dipolar moment induced in a freely rotating molecule subjected to an external magnetic field; this magnetizability is a tensorial quantity, of which the isotropic magnetizability is one third the trace of this tensor, calculated as a sum of diamagnetic and paramagnetic contributions [10] that are listed separately. For a free molecule there is likewise a tensor for the rotational *g* factor, which measures the extent to which a magnetic dipolar moment arises from the rotation of the molecule about its centre of mass; again obtained as one third the trace of the *g* tensor, the isotropic value listed is the sum of nuclear and electronic contributions, of which the latter have diamagnetic and paramagnetic components, all of which are listed separately. Of the last six rows, three contain the moments of inertia about the principal rotational axes, and another three rows present the corresponding rotational parameters.

Six further tables, one for each structural isomer of $^1H_2{}^{12}C^{14}N_2$ investigated except for cyanamide and isocyanamide combined into one table, present the calculated values of parameters pertaining to the optimized geometric structure of the atomic centres, as lengths of inferred chemical bonds or the smallest internuclear distances, and interbond angles, in a set sufficient to define unambiguously the geometric arrangement of atomic centres according to a specified point group. These tables include also the calculated wavenumbers of fundamental vibrational modes within specified symmetry classes, the corresponding calculated intensities, the calculated wavenumbers scaled by 0.95, and pertinent data from experiment for structure, wavenumber and intensity where available.

DISCUSSION

Relation Between Calculation and Experiment

Before discussing in detail the numerical results of our computational work, we describe the theoretical and computational context of the present calculations: apart from deficiencies of models employed in the analysis of experimental data, we must be aware of the limitations of both theoretical models and the computational aspects. Regarding theory, even a single helium atom is unpredictable [14] purely mathematically from an initial point of two electrons, two neutrons and two protons. Accepting a narrower point of view neglecting internal nuclear structure, we have applied for our purpose well established software, specifically Dalton in a recent release 2.0 [9], that implements numerical calculations to solve approximately Schrödinger's temporally independent equation, thus involving wave mechanics rather than quantum mechanics in other forms. The trial wave function for only the electrons is composed from basis functions in a chosen set, described as *aug-cc-pVTZ*, implying three gaussian functions to represent each ‘valence’ orbital, correlation-consistent and augmented with diffuse and polarization functions; although in principle a further set at the maximum theoretical level within Dalton 2.0, described as *aug-cc-pV6Z*, implying use of six gaussian functions analogously, is available for H, C and N atomic centres, the accessible computing resources precluded such use for all isomers: to maintain a common level of basis set for all isomers, we accepted the former set. In each basis function, the coefficient of a coordinate in an exponent is fixed, whereas the coefficient of each gaussian function in a fixed set is adjusted to yield a minimum energy of the selected molecular system. As those basis functions serve to mimic wave functions of an atom with one electron, further procedures serve to take into account, in a necessarily incomplete and approximate manner, repulsion and correlation between electrons. A further calculation of perturbational type has as its objective partially to take into account relativistic effects, of types mass velocity and Darwin, not encompassed directly in solution of Schrödinger’s equation; for atoms H, C and N these relativistic corrections are small, and vary little between the various structural isomers. The wave function that results from this calculation is an artefact of this approach to our application of quantum mechanics, for which reason we refrain from discussing any aspect of this artefact, or of its even more artefactual constituent basis functions; a molecular distribution of electronic density, which is in principle an observable quantity, can clearly not be decomposed uniquely into exponential or gaussian functions in a finite sum. As the criterion for an optimal wave function is the minimum total energy, both with optimized coefficients of basis functions and with optimized geometry, the resulting electronic density is subject to error reflecting an incomplete basis set; additional error results from an incomplete account of electronic correlation. Various molecular properties are customarily related to the electronic density and to the arrangement of the atomic nuclei, but a particular property might be sensitive to that density in particular regions of the effective molecular volume, such as near specific nuclei; for this and other reasons, the quality of calculation of each such property varies according to its nature, and some values of properties would then inevitably be nearer experimental values of these properties than others.

Apart from use of experimental values of atomic – rather than nuclear – and electronic masses and of electric charges, the basis of this calculation has an empirical component. The calculation is certainly not made genuinely from first principles or *ab initio*, firstly because the composition of the basis set is predetermined, by those who have published this basis set [12] and by the authors of Dalton software [11] who have incorporated it, according to its success in reproducing experimentally observable quantities and other calculated properties. Secondly, the solution of Schrödinger’s equation is based on a separation of electronic and nuclear motions, essentially with atomic nuclei fixed at relative positions, which is a further empirical imposition on the calculation; efforts elsewhere to avoid such an arbitrarily distinct treatment of subatomic particles, even on much simpler molecular systems, have proved only partially successful [15–17], at a greatly increased cost and complication of such calculation. With account taken concurrently of both nuclear and electronic motions, Schrödinger's equation has only recently been solved exactly for the hydrogen and other atoms [18]. A practical advantage of a separation of electronic and nuclear motions is that, on that basis, methods and algorithms have been well developed to estimate diverse molecular properties, even those such as the rotational *g* factor that partially transcend that approximation of separate treatment of electronic and nuclear motions [10]. According to that separate treatment, all molecules with the same formula and total charge represent local minima on a single hypersurface of potential energy, provided that all crossings of surfaces are avoided when a complete hamiltonian is applied. Although, to achieve a local minimum on an hypothetical hypersurface of potential energy in nine spatial dimensions applicable to the prospective motion of atomic nuclei, we undertook optimization of the relative coordinates of nuclear particles, with internuclear separations varied within an apparently small range from a specified initial conformation, there is within the progress of the calculation an implicit or explicit suppression of the seeking of a global minimum of energy; we become thereby able to distinguish these seven structural isomeric forms, among further possible, but thermodynamically less likely, isomers. As structural isomers of H_2CN_2 numbering six have been demonstrated to be sufficiently durable and stable to be characterized experimentally according to spectrometric measurements of various kinds, the separate treatment of electronic and nuclear motions that yields the corresponding classical structures in terms of geometric arrangements of atomic nuclei seems acceptable in the region of at least six of those minima on that putative hypersurface of potential energy; in regions not near those minima, such as those near the location of a *transition structure* that possesses one or more imaginary vibrational frequencies, such a separate treatment is questionable. Thirdly, a proper quantum-mechanical calculation is subject to requirements of indistinguishability of all identical particles, not just electrons; in the context of the present calculations there is neglect of permutation symmetry of the two atomic nuclei of both hydrogen, ^{1}H, and nitrogen, ^{14}N, that is contrary to that fundamental requirement of quantum mechanics.

As is typical of computer programmes for conventional calculations of molecular electronic structure and a resulting geometric conformation of relative nuclear positions and molecular properties, Dalton [11] provides no estimate of error or uncertainty in those internuclear separations or properties resulting from either numerical error or approximations in the method. Despite our use of the same basis set, *aug-cc-pVTZ*, for calculations on each structural isomer, there remains latitude in the conduct of the calculation according to the concept of a complete active space. That basis set is the largest for which our calculations, on the available hardware and within the limitations of Dalton, are practicable under the present conditions. Altering the number of electrons in that active space yields slight and apparently significant variations in internuclear distances and other descriptors of molecular properties of the types that we present in the several tables. Although we have accepted as the best wave function of each isomer the one among our extensive, but not exhaustive, tests that yielded the least total molecular energy, there is in general no monotonic trend of values of molecular properties, such as bond lengths or wavenumbers of characteristic vibrational modes, to converge to a limit well defined in the progress toward a converged total energy; the variation theorem is inapplicable to this process. Variation of the basis set would doubtless yield further slight variations of resultant molecular descriptors. As an exploratory test on only diazomethane, we made a calculation with the same basis set but with a further approximation of density functionals; the structural parameters and the properties, of those that the calculation permitted, varied slightly from those values obtained without this approximation. The total duration of a calculation with density functionals, but without all properties, was about two fifths that without this approximation.

Despite one's intent to compare calculated results with corresponding parameters deduced from experimental data, these quantities inherently defy direct comparison. In particular, the calculated structural parameters for an optimized structure pertain to a geometric arrangement of atomic centres in their relative equilibrium locations according to a local minimum on an hypothetical hypersurface of potential energy that is an artefact of a separate treatment of electronic and nuclear motions. Experimental data pertain either to these small molecules in particular quantum states, which have a completely indefinite geometric structure so effectively no extension in space or time and no correspondence to a classical structure [19], or to ensembles of molecules averaged over internal states occupied at a temperature of a particular experiment. For one to deduce accurately from experimental data, for instance from spectral data for transitions between discrete molecular states, the equivalent theoretical function of potential energy of a free molecule as a dependence on internuclear separations that is independent of nuclear masses, one must take into account the fact that electrons fail to follow perfectly the putative nuclear motions conventionally described as vibrational and rotational. To enable one to derive from spectral data a function purely for potential energy, an elimination of the effect of finite nuclear masses requires not only extensive spectral measurements on multiple isotopic variants but also application of corrections described as adiabatic and nonadiabatic, encompassed within adiabatic terms and rotational and vibrational g factors; this process, and in some cases also the effects of finite nuclear volumes, has been satisfactorily implemented for diatomic molecular species [20], but remains largely impracticable for polyatomic molecules; Dalton [11] nevertheless provides procedures for vibrational averaging based on an harmonic approximation. A comparison between geometric parameters obtained through a calculated molecular electronic structure and those from experiment must thus be necessarily rough. For other than an optimized structure, and particularly when the total electronic energy much exceeds that associated with the residual energy, known also as *zero-point energy*, within the most stable electronic state, the approximation of separate treatment of electronic and nuclear motions is subject to failure because multiple electronic states are likely to have comparable energies under those conditions, whether or not Dalton software indicates such a possibility.

For an optimized structure, the total electronic energy that Dalton yields, including effects of repulsion between atomic nuclei, is formally applicable to an isolated single molecule in its hypothetical equilibrium condition, which is neither a spectral nor a thermodynamic state; this energy is expressed most appropriately in SI units as joules, or aJ, per molecule. Even with an addition of residual energy, calculated from half the sum of vibrational wavenumbers of fundamental modes – harmonic or otherwise, such an energy still applies purely to an isolated molecule. Mere multiplication by Avogadro's constant to yield a nominal energy per mole is grossly misleading because a molar quantity implies a macroscopic sample in some state of aggregation. Under standard thermodynamic conditions, the state of aggregation varies with the structural isomer – diazomethane and diazirine are vapours at 300 K whereas cyanamide is an involatile solid – hence subject to particular conditions of at least pressure and temperature, and encompasses all energies of intermolecular interactions; such energies vary considerably with the intrinsic properties of individual molecules, such as the extent of polarity or molecular electric dipolar moment. Although these energies of intermolecular interactions under conditions applicable to standard thermodynamic states seem minuscule by comparison with total electronic energies, they become significant by comparison with small differences between energies of ideal molecular structural isomers, and likewise vary with the nature of each isomer. The variations in residual energy among these isomers are small but significant.

The electric dipolar moment derived from the Stark effect on molecular spectral transitions pertains formally to an expectation value of charge displacement over domains of internuclear separations and pertaining to particular quantum states, rather than representing that charge displacement for internuclear distances in a particular fixed set corresponding to an equilibrium conformation. Just as an atom within a molecule is poorly defined, the net atomic charge associated with a particular atomic centre is poorly defined both theoretically and experimentally: there are various possible methods both to calculate this quantity and to measure it, such as through diffraction by xrays and electrons, but the fundamental problem remains that in a molecule other than one with a single atomic nucleus there is no atom – only atomic nuclei and their associated electrons; any partition of total electronic charge is consequently arbitrary. Cioslowski's approach nevertheless yields estimates of redistribution of electronic charge on formation of a molecule, such as those listed in Table 16-1, that exhibit satisfactory properties [13]; although one might seek to apply such data to reinforce conventional notions of chemical binding and to indicate prospective modes of chemical reactivity, we refrain from such speculation. Reported in Table 16-1, these estimates described as atomic populations are first derivatives of the electric dipolar moment of a molecule with respect to cartesian coordinates [13], which differ significantly from any attempted integration of electronic charge in a chosen volume about one nucleus minus the nuclear charge or atomic number.

Like electric dipolar moment, the magnetic and other electric, properties of molecules deduced from spectral experiments pertain inevitably to expectation values over domains of internuclear separations; the calculated values, listed in Table 16-1, might however serve as approximate guides to what experiments might provide. The rotational parameters deduced from experiment are supposed to be inversely proportional to inertial parameters on the basis of a classical interpretation of a rigid assemblage of atomic nuclei and their directly associated electrons according to separate atomic masses. The distinction between calculated moments of inertia, and rotational parameters derived therefrom, and the corresponding experimental quantities, suffers from the same fundamental impediment as the parameters of geometric structures. In all cases only a rough comparison is formally practicable, but the trends of deviations between calculated and measured properties might provide guidance for the conduct and interpretation of future experiments.

Vibrational mode pose a particular dilemma for comparison of calculated and experimental quantities. The latter are derivable with great relative precision, from about one part in 10^3, in the worst cases of vibration-rotational bands with unresolved contours for a compound among the present seven observed as a gaseous sample, to about one part in 10^7, such as for band ν_7 of carbodiimide [21] in Table 16-4 for which a full rotational analysis proved practicable. Calculations of molecular electronic structure in Dalton and similar computational procedures yield wavenumbers according to a parabolic dependence of small displacements from the equilibrium conformation, which pertain thus to hypothetical harmonic vibrations. Any cross section of a postulated hypersurface of potential energy accurately deduced from experimental data according to a classical model lacks an exactly parabolic profile, even near a local minimum of energy of which our calculations confirm seven for these isomers of H_2CN_2; for this reason there is a systematic deviation between directly calculated vibrational wavenumbers and those measured for centres of vibration-rotational bands in infrared spectra or Raman scattering. To take into account this condition, an empirical method of adjusting the calculated wavenumbers involves scaling, by a value typically $\approx$0.95; such a value has formal justification for application to stretching modes involving hydrogen atomic centres [22], but for other modes is merely a convenient factor. To facilitate comparison between experimental and calculated wavenumbers, we apply this scaling factor in the tables for individual structural isomers. The variability of calculated wavenumbers associated with particular fundamental vibrational modes seems to be as much as ten per cent depending on the conditions of the calculation apart from the particular basis set, namely the number of electrons in the active space. Measurement of absolute intensities of vibration-rotational bands of polyatomic molecules is difficult, and the results are hence typically much less precise than for wavenumbers of band centres; for instance, about one part in ten has been achieved for diazomethane [23], whereas for some diatomic molecules [20] one part in 10^2 is typically achievable. Incompletely resolved separate lines assigned to individual vibration-rotational transitions and overlapping bands of separate vibrational modes complicate these measurements for polyatomic molecules. As presented in Tables 16-2–16-7, calculated intensities are obtained from dipolar gradients of atomic centres, also known as

Table 16-2. Calculated and experimental, structural and vibrational parameters of diazomethane (point group C_{2v}): calculated and measured lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, scaled wavenumbers, and experimental wavenumbers and intensities[a]

	calc.			exp.	
internuclear distance/10^{-10} m, C-H	1.064			1.075	
internuclear distance/10^{-10} m, C-N	1.304			1.300	
internuclear distance/10^{-10} m, N-N	1.113			1.139	
interbond angle/deg, H-C-H	126.2			126	
vibrational mode	ν/m^{-1} calc.	$I/10^{-21}$ m calc.	ν/m^{-1} scaled	ν/m^{-1} exp.	$I/10^{-21}$ m exp.
ν_1, a_1	334084	20.59	317380	307710	7.6
ν_2, a_1	210522	897.74	199996	210157.7	284.5
ν_3, a_1	153722	66.75	146036	141333	19.9
ν_4, a_1	117275	1.80	111411	117700	5.1
ν_5, b_1	57590	26.35	54711	56819	
ν_6, b_1	39225	208.38	37264	40887	
ν_7, b_2	347807	1.81	330417	318450	
ν_8, b_2	117355	6.55	111487	110900	0.2
ν_9, b_2	41596	0.87	39516	41579	58.9
residual energy/*hc*	709588		674109	672945	

[a] For references to sources of experimental data, see the text.

net atomic charges or the atomic polar tensor listed in Table 16-1; as these charges vary appreciably with the nature of the particular basis set and other aspects of the calculation, there is no expectation of great absolute accuracy of the resulting intensities, but relative values might serve for comparison with experimental data.

The extent of information from experiment about the quantitative aspects of molecular geometry and properties varies with the particular structural isomer; 1,2-diazirine is not yet positively detected from experiments, whereas much information about chemical and physical properties is known about diazomethane and 1,1-diazirine, with other isomers in intermediate conditions. Those two specified isomers are not the most stable, but the inversion motion of the amino moieties in both cyanamide and isocyanamide greatly impedes efforts to define structural parameters of these molecules from their spectra, apart from the more difficult conditions in working with these involatile substances. As little or no experimental thermochemical data are available for these isomers, we compare our order of relative stabilities with those of Hart [2], of Kawauchi et al. [7] and of Moffat [3]. As a concession to such comparison on a molar basis, we present in Table 16-1 our total energies including the scaled residual energy on a molar basis; Figure 16-1 depicts these energies for the seven selected structural isomers. All these authors agree that cyanamide is most stable, with carbodiimide next except for Hart [2]; other than our finding isocyanamide to be least stable, our order of stability of the

Table 16-3. Calculated and experimental, structural and vibrational parameters of cyanamide and isocyanamide (both point group C_s): calculated and measured lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, scaled wavenumbers, and experimental wavenumbers[a]

	cyanamide calc.		exp.		isocyanamide calc.		
internuclear distance/10^{-10} m, N-H	1.016		1.001		0.998		
internuclear distance/10^{-10} m, C-N	1.355		1.346				
internuclear distance/10^{-10} m, C-N	1.164		1.1645		1.162		
internuclear distance/10^{-10} m, N1-N2	2.518		2.506		1.355		
interbond angle/deg, H-N-H	109.5				109.7		
interbond angle/deg, N-C-N or N-N-C	177.4				169.7		
vibrational mode	ν/m^{-1} calc.	$I/10^{-21}$ m calc.	ν/m^{-1} scaled	ν/m^{-1} exp.	ν/m^{-1} calc.	$l/10^{-21}$ m calc.	ν/m^{-1} scaled
ν_1, a′	376526	74.73	357700	342000	372518	26.04	353892
ν_2, a′	242694	115.84	230559	227000	231498	98.50	219923
ν_3, a′	177238	70.90	168376	157500	180127	43.04	171121
ν_4, a′	111059	11.34	105506	105500	112634	89.15	107002
ν_5, a′	69328	359.94	65862	71386	98279	130.42	93365
ν_6, a′	31683	8.71	30099	38000	26130	2.29	24824
ν_7, a″	386150	107.09	366843	348000	381627	62.70	362548
ν_8, a″	128174	0.82	121765	72000	144691	11.01	137458
ν_9, a″	32353	0.50	30735		10769	4.82	10231
residual energy/*hc*	777602		738722		779136		740179

[a] For references to sources of experimental data, see the text.

Table 16-4. Calculated and experimental, structural and vibrational parameters of carbodiimide (point group C_2): calculated and measured lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, scaled wavenumbers, and experimental wavenumbers[a]

	calc.		exp.	
internuclear distance/10^{-10} m, N-H	0.997		1.0039	
internuclear distance/10^{-10} m, C-N	1.233		1.2247	
interbond angle/deg, H-N-C	116.7		119.1	
interbond angle/deg, N-C-N	171.5		171.6	
angle/deg, HN..NH	88.5		89.35	
	ν/m^{-1}	$I/10^{-21}\,\mathrm{m}$	ν/m^{-1}	ν/m^{-1}
vibrational mode	calc.	calc.	scaled	exp.
ν_1, a	380037	65.95	361035	349800
ν_2, a	123820	0.10	117629	128500
ν_3, a	102125	23.93	97019	
ν_4, a	78250	106.49	74338	
ν_5, a	53179	0.04	50520	53700
ν_6, b	379817	241.55	360826	
ν_7, b	217176	1017.52	206317	210470.47
ν_8, b	97604	864.55	92724	89000
ν_9, b	52298	137.13	49683	53700
residual energy/*hc*	742153		705045	

[a] For references to sources of experimental data, see the text.

Table 16-5. Calculated and experimental, structural and vibrational parameters of nitrilimine (point group C_1): calculated and measured lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, scaled wavenumbers, and experimental wavenumbers[a]

	calc.			
internuclear distance/10^{-10} m, C-H	1.069			
internuclear distance/10^{-10} m, C-N	1.192			
internuclear distance/10^{-10} m, N-N	1.270			
internuclear distance/10^{-10} m, N-H	1.006			
interbond angle/deg, H-C-N	128.5			
interbond angle/deg, C-N-N	167.6			
interbond angle/deg, N-N-H	106.6			
	ν/m^{-1}	$I/10^{-21}\,\mathrm{m}$	ν/m^{-1}	ν/m^{-1}
vibrational mode	calc.	calc.	scaled	exp.
ν_1, a	365122	21.77	346866	325010
ν_2, a	339346	17.12	322379	314250
ν_3, a	206186	574.09	195877	203270
ν_4, a	146618	162.63	139287	127810
ν_5, a	117182	18.27	111323	118750
ν_6, a	92333	55.35	87716	79210
ν_7, a	80640	0.89	76608	60650
ν_8, a	50203	28.52	47693	46140
ν_9, a	40669	18.01	38636	
residual energy/*hc*	719149		683192	

[a] For references to sources of experimental data, see the text.

Table 16-6. Calculated and experimental, structural and vibrational parameters of l,l-diazirine (point group C_{2v}): calculated and measured lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, scaled wavenumbers, and experimental wavenumbers[a]

	calc.		exp.	
internuclear distance/10^{-10} m, C-H	1.069		1.0803	
internuclear distance/10^{-10} m, C-N	1.493		1.4813	
internuclear distance/10^{-10} m, N-N	1.181		1.228	
interbond angle/deg, H-C-H	120.2		120.5	
interbond angle/deg, N-C-N	46.6		48.98	
	ν/m^{-1}	$I/10^{-21}$ m	ν/m^{-1}	ν/m^{-1}
vibrational mode	calc.	calc.	scaled	exp.
ν_1, a_1	328440	15.58	312018	302325
ν_2, a_1	197881	57.99	187987	162300
ν_3, a_1	159980	2.85	151981	145916.06
ν_4, a_1	101627	3.36	96546	99180
ν_5, a_2	102244	0	97132	96270
ν_6, b_1	104115	57.32	98909	96730
ν_7, b_1	83864	21.77	79671	80713.95
ν_8, b_2	340757	21.09	323719	313190
ν_9, a_2	119200	6.87	113240	112491.43
residual energy/*h*c	769054		730102	704558

[a] For references to sources of experimental data, see the text.

Table 16-7. Calculated structural and vibrational parameters of 1,2-diazirine (point group C_1): calculated lengths of bonds and interbond angles; calculated wavenumbers and intensities of fundamental modes, and scaled wavenumbers

	calc.		
internuclear distance/10^{-10} m, C-H_a	1.070		
internuclear distance/10^{-10} m, C-N_a	1.390		
internuclear distance/10^{-10} m, C-N_b	1.254		
internuclear distance/10^{-10} m, N_a-N_b	1.749		
internuclear distance/10^{-10} m, N-H_a	1.029		
interbond angle/deg, H-C-N	136.7		
interbond angle/deg, H-N-N	108.3		
interbond angle/deg, N-C-N	82.7		
	ν/m^{-1}	$I/10^{-21}$ m	ν/m^{-1}
vibrational mode	calc.	calc.	scaled
ν_1, a	338430	2.40	321509
ν_2, a	331928	2.05	315332
ν_3, a	171791	3.84	163201
ν_4, a	137330	9.11	130464
ν_5, a	129595	70.05	123115
ν_6, a	111071	46.51	105517
ν_7, a	98527	68.03	93601
ν_8, a	81647	47.30	77565
ν_9, a	45464	7.51	43191
residual energy/*hc*	722891		686746

other isomers agrees with that of Kawauchi et al. [7] Our estimate of the energy of carbodiimide relative to cyanamide is larger than the value 15.1 kJ mol^{-1} [24] deduced from experiments in which both species appeared to coexist in thermodynamic equilibrium. Vincent and Dykstra [25] calculated the difference of energies of cyanamide and isocyanamide to be 220 kJ mol^{-1}; that difference, smaller than ours, might reflect their less sophisticated level of calculation. Of five acyclic isomers, Hart [2] found isocyanamide second in stability; his order of the other four acyclic isomers is the same as ours.

As little or no experimental information is available for electric and magnetic properties other than electric dipolar moment, we make a general comparison here. With regard to electrical properties in Table 16-1, all structural isomers have electric dipolar moments in a moderate range, which facilitates detection of these species through pure rotational transitions in microwave spectra; for a species not yet so observed, 1,2-diazirine, the rotational parameters provided in this table enable rough prediction of frequencies and intensities of such transitions. The vibrational polarizability for the various structural isomers has a generally positive sign, but the magnitudes of components of this tensor vary considerably. For nitrilimine we omit from this table calculated values of vibrational polarizability, and the corresponding vibrational contribution to total molecular polarization, because these calculated values have uncharacteristically large magnitudes; for only this isomer the number of vibrational modes resulting from the calculation is eleven, including two spurious modes with small wavenumbers corresponding essentially to rotational motion; such effects, resulting from slight deficiencies of calculations of molecular electronic structure, are known to corrupt estimates of vibrational polarizability. Use of other active spaces for nitrilimine failed to eliminate these deficiencies.

For the rotational g tensor, the nuclear contribution to the isotropic value varies among isomers in a small range 0.68 – 0.72 for acyclic isomers but is essentially the same, at 0.594, for the two cyclic isomers. In all cases both the diamagnetic and paramagnetic electronic contributions are negative; the magnitude of the diamagnetic component, in a small range 0.04 – 0.06, is much smaller than the magnitude of the paramagnetic component, which varies in a range 0.5 – 1 for these compounds at calculated equilibrium geometries. Depending on the relative magnitudes of electronic and nuclear contributions, the net effect, reflected in the isotropic g value, is therefore positive or negative. Wilson et al. [26] reported generally negative values of diagonal components of this tensor for many small molecular species, with differences between calculated and experimental values typically less than 3 per cent. As a result of their calculations for 61 compounds with a further density-functional approximation, Wilson et al. concluded [26] that calculations of such magnetic properties are generally reliable; that conclusion is expected to be applicable to our results of analogous calculations without that approximation, provided that these calculations involve a satisfactory basis set and sufficient account of electronic correlation. Like the isotropic rotational g factor, the isotropic magnetizability has diamagnetic contributions, in all cases negative and near -1.8×10^{-27} J T^{-2} for acyclic isomers or near $-1.4 \times 10^{-27}\,\mathrm{J\,T^{-2}}$ for cyclic isomers; the paramagnetic contributions are in all cases positive and near $1.4 \times 10^{-27}\,\mathrm{J\,T^{-2}}$ for acyclic isomers and $1.1 \times 10^{-27}\,\mathrm{J\,T^{-2}}$ for cyclic isomers. The net effect is consequently in a range/$10^{-28}\,\mathrm{J\,T^{-2}}$ from −3.1 to −4.6.

For other properties we discuss results separately for the various structural isomers of ${}^{1}H_2{}^{12}C{}^{14}N_2$.

Diazomethane

For this species we constrained our calculation to retain a planar conformation belonging to point group C_{2v}, in accordance with experimental evidence; the calculations on that basis yielded no imaginary vibrational wavenumbers that would indicate a decreased symmetry. Although such a constraint of symmetry is superfluous in such a calculation, its presence greatly diminishes the duration of calculation and the extent of storage space for integrals. The calculated electric dipolar moment, listed in Table 16-1, is comparable with the experimental quantity, $5.0 \times 10^{-30}\,\mathrm{C\,m}$ [27], but no experimental values are available for comparison with our magnetic quantities. The rotational parameters that we calculated, according to Table 16-1, differ slightly from the corresponding experimental quantities/m^{-1} for the vibrational ground state, $A = 910.5603$, $B = 37.7108452$ and $C = 36.1757609$ [28]. In view of the qualifications, stated above, about a general comparison between calculated and experimental geometric parameters, the calculated lengths of chemical bonds are reasonably similar to experimental values, compared in Table 16-2. The scaled values of vibrational wavenumbers are generally nearer the experimental quantities [29–31] than the unscaled values. According to a single calculation for diazomethane using density functionals, those resulting vibrational wavenumbers would clearly benefit from a different scaling factor; there seems to be no decisive gain of accuracy of prediction from use of such density functionals, although that approach might decrease somewhat the total duration of calculation. The calculated intensities of vibrational transitions in fundamental modes of class a_1 have magnitudes in the same order as the experimental values [23], but for modes of class b_2 the disagreement is great; as all these experimental values were obtained from spectra at only moderate resolution, their reliability is questionable.

Cyanamide and Isocyanamide

Because their structures, differing only in the orientation of the cyano moiety with respect to the amino moiety, are similar, these two isomers that belong to the same point group, C_s, we conveniently consider together. According to our calculations, cyanamide and isocyanamide represent the most and least stable, respectively, of the seven selected isomers, and are the two most polar molecules, reflecting the natures of their constituent amino and cyano moieties. The atomic nuclei of both cyanamide and isocyanamide undergo a motion, inversion at the nitrogen atom of the amino moiety, of large amplitude, with which is associated a double minimum in the function for potential energy; for this reason the rotational parameters in the vibrational ground state comprise two sets, one for each state of the symmetry pair [21, 32]. Much more experimental information exists for cyanamide than for isocyanamide.

For cyanamide, the components of electric dipolar moment/10^{-30} C m parallel to inertial axes are $p_a = 14.14$ and $p_c = 3.03$ [33], slightly larger than our calculated values $p_a = 13.33$ and $p_c = 2.878$; the total moment from experiment is 14.46×10^{-30} C m, correspondingly larger than our calculated value in Table 16-3. We compare our calculated rotational parameters with the effective rotational parameters/m^{-1} for the vibrational ground state – $A = 1041.19325$, $B = 33.78923475$ and $C = 32.90918052$ [34], which are all a little larger than the calculated values. Our calculations indicate that both these isomers have a non-linear spine, consistent with experiment for both structural isomers; those calculated internuclear distances, in Table 16-3, agree satisfactorily with the values deduced from experiment for cyanamide.

For isocyanamide, spectral data of insufficient isotopic variants have been obtained to enable the derivation of experimental structural parameters; although application of the Stark effect to split spectral lines of a single isotopic species would suffice to yield values of the total electric dipolar moment and its two non-zero components, this experiment has not been reported. We compare our calculated rotational parameters with the effective rotational parameters/m^{-1} for the vibrational ground state $-A = 654.831$, $B = 34.16822$ and $C = 33.05467$ [35], from a mean of corresponding parameters for the two inversion states of least energy; the large difference between calculated and experimental values of A results from the large amplitude of wagging motion in these inversion states that is not taken into account in our calculation involving static relative nuclear positions. Our calculated values of other spectral and structural properties of isocyanamide are likely as near prospective experimental values as their counterparts for cyanamide.

Carbodiimide

According to data from microwave spectra of carbodiimide [24], the electric dipolar moment/10^{-30} C m is 6.34, somewhat smaller than the calculated value in Table 16-1; the rotational parameters/m^{-1} are $A = 1265.02346$, $B = 34.5803859$ and $C = 34.5775333$ [24], also larger than the calculated values. In Table 16-4, one highly accurate vibrational wavenumber is known, for mode ν_7 from spectra of gaseous samples [21], but other data emanate from spectra in solid phases [36]; the intensity that we calculated for the specified vibrational mode is large, consistent with the corresponding band being most readily observed in a spectrum of a gaseous sample, but two intensities, both small, are calculated for vibrational modes that seem to have been observed for solid samples, in which molecules are subject to significant intermolecular interactions.

Nitrilimine

As the only experimental observations of this isomer, apart from a possibly ambiguous signal in a mass spectrum [37], are vibrational absorption features attributed to its dispersion in solid argon [8], no measured properties correspond to any calculated result in Table 16-1 for this species, but Table 16-5 includes those vibrational data. The calculated angle between C—N and N—N bonds is approximately the same as for isocyanamide; the structure of nitrilimine differs from that of isocyanamide through transfer of one hydrogenic atomic centre from the terminal N to the terminal C. The angle between the C—H and N—H bonds is calculated to be 92°, similar to the angle between the two N—H bonds of carbodiimide.

1,1-Diazirine and 1,2-Diazirine

Of these two cyclic structural isomers, for diazirine the electric dipolar moment is known from the Stark effect in microwave spectra [38] to be 5.3×10^{-30} C m, somewhat smaller than the calculated value in Table 16-1. All calculated net atomic charges for diazirine have small magnitudes. The rotational parameters/m^{-1} for the vibrational ground state – $A = 136.59901$, $B = 78.9478949$ and $C = 55.7923163$ [39] – are comparable with the calculated values in Table 16-1. Some fundamental vibrational modes, as listed in Table 16-6, have wavenumbers well defined directly from experiment [40], whereas the wavenumber of ν_5 for the CH_2 twisting mode, being infrared inactive, is estimated through a force field fitted to many data for isotopic variants [40]. The wavenumber of ν_2 for the N=N stretching mode is overestimated in our calculation, consistent with a length of this bond smaller than from experiment. The scaled wavenumbers for the C—H stretching modes are still appreciably larger than the direct experimental values, but seem comparable with 'harmonic band centres' from the same fitted force field [39]; the scaled wavenumbers associated with the other six fundamental modes are comparable with the experimental data. As the energy of 1,2-diazirine is only slightly greater, according to Table 16-1, than that of nitrilimine, which has been formed by photolysis of a suitable precursor in solid argon [8], there is a prospect that 1,2-diazirine might likewise be prepared and stabilized in such an environment. We find, in Table 16-7, the length of a C—N bond at 1.75×10^{-10} m to be atypically large, in accordance with other large values in the first calculation [3] and subsequent work, but there is no indication through imaginary vibrational wavenumbers that the converged geometry pertains to a transition structure. There is a possibility of two geometrical isomers of this cyclic molecule, with both hydrogens on the same or different sides of the ring defined by the massive atoms; because the hydrogen attached to carbon is near the plane of that ring, the difference of energies is likely to be small.

CONCLUSION

By means of these pragmatic calculations on structural isomers of formula $^{1}H_2{}^{12}C^{14}N_2$, we have shown examples of the information of kinds that one might derive with contemporary software for quantum-chemical calculations of molecular electronic structure, namely some electric and magnetic properties, beyond the optimized geometric structures of equilibrium nuclear conformations and wavenumbers of vibrational modes. For this purpose we have applied a particular computer program, although one expects that our results would be closely reproduced with alternative computer programs and the same level of theory, providing that all users have conformed to appropriate conventions. To compare with experimental data is difficult because in all cases the quantities that one can calculate for a single sample species differ from what might be observed directly from experiments, and corrections of neither experimental data nor calculated results for equilibrium structures of polyatomic molecules are sufficiently developed to facilitate such comparison in a routine manner for such polyatomic molecules. In general, the experimental and theoretical models are intrinsically somewhat incompatible. Even for these small molecules, encompassing only five atomic nuclei of small atomic number and their 22 associated electrons, these calculations, and by implication analogous calculations on other systems involving more than two nuclei and two electrons, remain partially an art rather than an exact science, and a guide to prospective information that critical experiments might provide, rather than a standard to which experiments must aspire. This guidance is nevertheless helpful in the planning of experiments and in their interpretation; within the formal limitations of the circumstances of the generation of these results as we have discussed, their relative trends provide qualitative, or at best semi-quantitative, information about properties, structural or other, according to a conventional and classical notion of molecular structure.

These calculations have all been based on an orbital model, even though eventually each orbital became replaced with, and approximated by, three gaussian functions. Even for methods involving density functionals, an orbital basis is still essential because no alternative method of calculating required integrals has been devised. In principle, rather than using a function of form $e^{-\alpha R}$ like that for an s orbital or $e^{-\beta R^2}$ as a gaussian function, one might use functions of forms γ (R_0-R) or δ $R(R_0-R)$ as products with Heaviside functions; although many of these functions, with varied values of parameters γ, δ and R_0 corresponding to coefficients α or β in the exponential functions, would undoubtedly be required to replace a particular exponential function, the tedious numerical integrations would be entirely or largely eliminated – indeed most might be replaced by simple algebraic formulae subject to highly efficient computation. The point is that the power of these calculations of molecular structure and properties, attested by the moderate agreement between calculated and experimental values in the preceding tables, reflects the enormous capacity of contemporary computer processors and memories rather than any particular resemblance between members of a basis set and solutions of Schrodinger's equation for an atom with one electron; such a solution defines an orbital. The latter solution, which may be made mathematically exact and algebraic, depends on a function for potential energy that comprises precisely only an electrostatic attraction between a single electron and an atomic nucleus, or even multiple atomic nuclei in a specified geometric arrangement. For even two electrons in the field of a single nucleus, a solution of such an exact and algebraic nature is impossible – the ‘many-body problem’; the direct application of orbitals, derived for a system of one electron, to systems with multiple electrons is formally illogical, because one thereby takes into account all attractions to one or other nucleus but neglects the repulsion between each two electrons. In an actual calculation with standard software, such as Dalton, the latter deficiency is approximately remedied first by use of a self-consistent field and then by further account of electronic correlation according to various methods. Such remedies would be equally applicable in the use of these functions of forms $\gamma\ (R_0\text{–}R)$ and $\delta R\ (R_0\text{–}R)$ with their Heaviside factors. No particular effects of the results of the latter calculations as molecular properties would hence be attributable to orbitals because no orbitals would be involved in the calculation: there need be no attempt to mimic orbitals in the generation of the latter functions – one would simply proceed according to an entirely numerical protocol with the variation theorem until attaining the desired convergence and numerical accuracy. Although orbitals play an enormous – excessive – role in the teaching and practice of contemporary pure chemistry, they are, and remain, artefacts of a particular approach to quantum mechanics. Matrix mechanics has never been sufficiently developed to be competitive with wave mechanics for application to such electronic systems – perhaps we can blame the physicists of a century ago for their ignorance of linear algebra relative to their knowledge of differential equations, but an effort to rectify that imbalance in the development of matrix mechanics seems unforthcoming in the foreseeable future. There have even been efforts to rationalize purported direct experimental observations of orbitals [41], which appear futile because of their lack of physical existence [42]. Despite the demonstrated equivalence of matrix mechanics and wave mechanics in a context of pioneer quantum mechanics [43], Dirac proved Schrodinger’s formulation to be grossly deficient with respect to Heisenberg’s formulation at a more profound level of theory [44]. Quantum mechanics must be considered to be not a chemical, not even a physical, theory – where is the physics in considering momentum to be, or to be represented by, a matrix according to matrix mechanics, or to be or to be represented by $-i\hbar\ \partial/\partial q$ according to wave mechanics, or to be or to be represented by a difference of creation and destruction operators devised by Dirac? – but a collection of mathematical methods, more or less consistent and of varied degree of sophistication and complication, to calculate some property or quantity – most meaningfully an observable property – but only approximately except for the most prototypical and simple systems of only indirect chemical interest. Notwithstanding such reservations, to model the electronic density in molecules one can profitably apply orbitals, or their representatives, in calculations of a sort with conventional software that we here apply to these isomers of diazomethane.

Since Coulson's time, substantial progress has been made towards approaching a quantitative status of results of quantum-chemical calculations within the scope of a separate treatment of electronic and nuclear motions as a working model. As the present results indicate, much further work is required to attain that objective, such as improving and extending both basis sets and the software that incorporates these functions up to the still expanding limits of computer hardware, improving the algorithms for taking into account the purported vibrational motion – not merely in an harmonic approximation, increasing the range of molecular properties accessible within a particular calculation, and refining both experimental and theoretical models to improve their compatibility.

ACKNOWLEDGEMENTS

JFO thanks Dr. R. D. Harcourt, Dr. R. Kobayashi and Dr. D. J. D. Wilson for helpful advice and information, and Professors M. and B. P. Winnewisser for providing relevant publications; Swinburne University of Technology and its Faculty of Information and Communication Technologies through a Research and Development Grant supported his visit to Melbourne to conduct this project, and the Australian Partnership for Advanced Computing provided use of the National Supercomputing Facilities.

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