

HIGHLY STRAINED SINGLE AND DOUBLE BONDS

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Abstract - The infrared spectra of the strained single bond compounds, [2.2.1]propellane, [2.1.1]propellane and [1.1.1]propellane, and the vibrational and electronic spectra of the strained bridgehead double bond compounds, adamantene and azahomoadamantene, are reported and discussed.

INTRODUCTION

Compounds containing very highly strained bonds have been of considerable interest for some time, but until relatively recently some of the most interesting ones were only characterized indirectly as fleeting intermediates in chemical reactions by trapping experiments. The introduction of flash photolysis and of low-temperature matrix isolation techniques permit their direct spectroscopic observation and thus a far more thorough testing of the limits of the current concepts of chemical bonding. Some of the most highly strained single carbon-carbon bonds are found in small-ring propellanes (1,2), while some of the most highly strained double carbon-carbon bonds occur at the bridgeheads of polycyclic hydrocarbons (2,3). In the present report, the spectroscopic properties of several new members of these two classes of compounds will be briefly described.

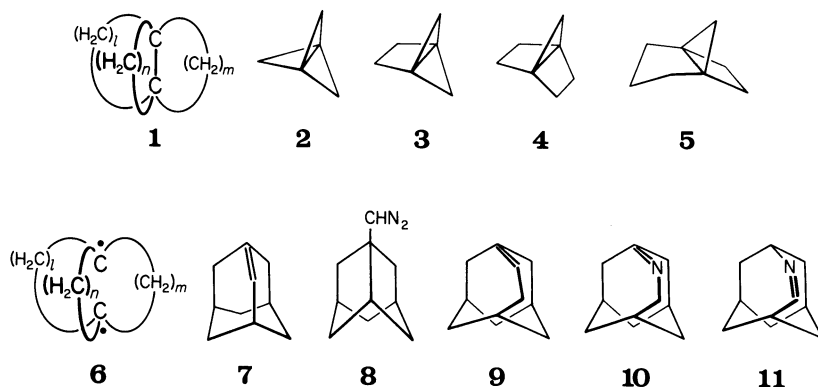
SMALL-RING PROPELLANES

[1.m.n]Propellanes are molecules of the general structure **1**. While those members of the propellane family which contain only unstrained rings are not particularly different from other saturated hydrocarbons, those containing several four-membered or three-membered rings are highly strained. Recent syntheses of the remaining small-ring propellanes from the bridgehead dihalides using *t*-butyllithium in solution (4) or metal atom vapors (5,6) enable us to study their spectra.

As the size of the rings decreases, the bonds at the bridgehead carbons of a propellane begin to deviate from the normal tetrahedral arrangement, in which the angles between the central bond and the three other bonds originating at the bridgehead are $109^{\circ}28'$. In [2.2.2]propellane the angles should be about 90° , and in the limiting case of [1.1.1]propellane (**2**), only about 60° . Such an inverted geometry at the bridgehead carbons must lead to a high strain energy. It is perhaps natural to expect the strain energy to increase as the angles decrease, and furthermore, to associate higher strain energy with higher reactivity.

This has now been found to be incorrect, and indeed, [1.1.1]propellane **2** is isolable (4) and far more stable than [2.1.1]propellane **3** (5) and [2.2.1]propellane **4** (6), which have so far only been obtained in matrix isolation, and even than the isolable [3.2.1]propellane **5** (7), [3.1.1]propellane (8) and [4.1.1]propellane (9). Unlike **2**, the others are sensitive to oxygen and tend to polymerize. Judging by the properties of a simple derivative (10), [2.2.2]propellane is unstable as well and undergoes a monomolecular 2+2 retrocycloaddition readily at room temperature, while **2** has a half-life of about 5 min at 114°C (4). In propellanes containing one or two three-membered rings, 2+2 retrocycloaddition is made relatively difficult as a general rule, presumably because the three-membered rings resist the necessary extension of the central bond. Then, the dominant reaction mode is intermolecular: an attack on the bridgehead carbon from the "unprotected" side, with simultaneous

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rupture of the central C-C bond. The ease of attack should be at least loosely related to the strength of this bond, i.e., to the energy difference between the propellane **1** and the biradical **6** in which the central bond has been lost.

The rupture of the central bond is promoted by the associated relief of strain energy. At the 6-31G* level of SCF theory, the strain energies of **2**, **3** and **4** are nearly identical: 103, 106, and 108 kcal/mol, respectively. This is not unusual for a series of compounds differing only by substitution of four-membered by three-membered rings; after all, the strain energy of cyclobutane (27 kcal/mol) is almost equal to that of cyclopropane (28 kcal/mol), and bicyclo[2.1.0]pentane has about the same strain energy as bicyclo[2.2.0]hexane (11). On the other hand, the strain relief upon rupture of the central bond is vastly different in the three propellanes: it is huge in the case of **4**, since the norbornane skeleton contains only five-membered rings and is relatively unstrained, substantial in the case of **3**, and smallest in the case of **2**, since the [1.1.1]bicyclopentane moiety is still very severely strained. The values for the strain relief calculated at this level of SCF theory are 94, 69, and 36 kcal/mol, respectively, and even if they are not quantitatively accurate, they indicate clearly that (i) the central bond in **4** has essentially no strength at all and may well have a negative bond energy (its calculated stretching force constant is an order of magnitude weaker than a usual C-C stretching force constant), (ii) the central bond in **3** is very weak, and (iii) the central bond in **2** is reasonably strong. It is an interesting question to ask to what degree other properties of the central C-C bond such as its electron density distribution reflect the different bond energies, since the latter may well be due primarily to differences in the strain energies of the biradical reference points rather than to any intrinsic properties of the unperturbed central bond itself.

It seems likely that it will take a while before the bonding in these small-ring propellanes is fully understood. A normal mode analysis would represent a helpful step towards this goal. The infrared spectra of a series of propellanes have now been recorded (4-6) and those of **2**, **3**, **4**, and **5** are presented in Fig. 1. They were taken in an argon matrix with the exception of the spectrum of the very stable propellane **2**, which was recorded in CS_2 solution, so that certain parts of the spectrum are blocked by solvent absorption. Figure 2 shows the frequencies, intensities, and symmetries of the ir transitions calculated for the two smallest propellanes by the MNDO (12) method. Although the agreement of the observed and calculated spectra is far from quantitative, their general similarity permits an assignment of at least some of the observed transitions to individual normal modes. Several among these assignments are obvious in all of the propellanes in Fig. 1, such as the C-H stretching vibrations of the methylene groups in the cyclopropane rings, which appear at the nearly constant frequencies of 3000 cm^{-1} (symmetric) and 3060 cm^{-1} (antisymmetric), respectively, almost the same as in cyclopropane itself. The most striking feature of the spectra is the presence of an intense band at a fairly low frequency. Its observed frequency increases as the ring size decreases: **5**, 515 cm^{-1} ; **4**, 530 cm^{-1} ; **3**, 574 cm^{-1} ; **2**, 603 cm^{-1} . It is assigned to an antisymmetric combination of peripheral C-C bond stretches and can be viewed as a "bobbing" mode in which the two bridgehead atoms move up and down in unison relative to the plane of the three peripheral carbon atoms in **2** and an analogous plane of the other propellanes, while the hydrogen atoms move as a counterpoise (Fig. 3). Isotopic substitution and Raman work are necessary before the vibrational analysis can be completed.

The optimized bond lengths of the propellanes calculated using the ab initio and MNDO methods are compared in Fig. 4. They are mostly strikingly normal, revealing relatively little of the misery in which these molecules find themselves.

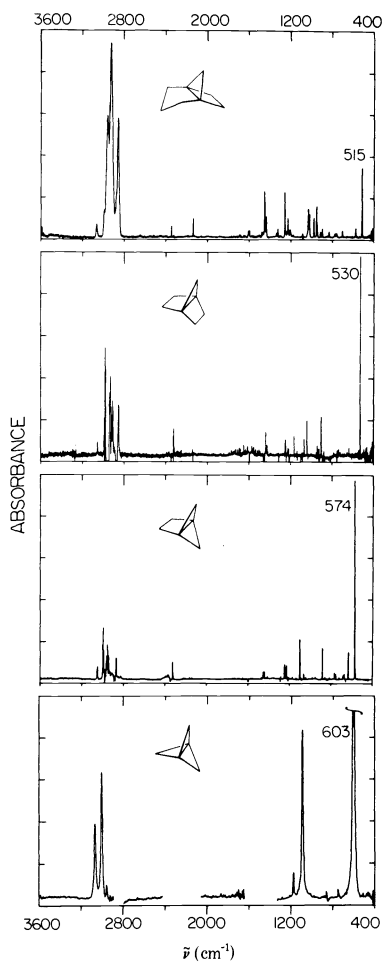


Fig. 1

Fig. 1. Observed infrared absorption spectra of propellanes. Solution in CS_2 (**2**) and argon matrix (**3,4,5**).

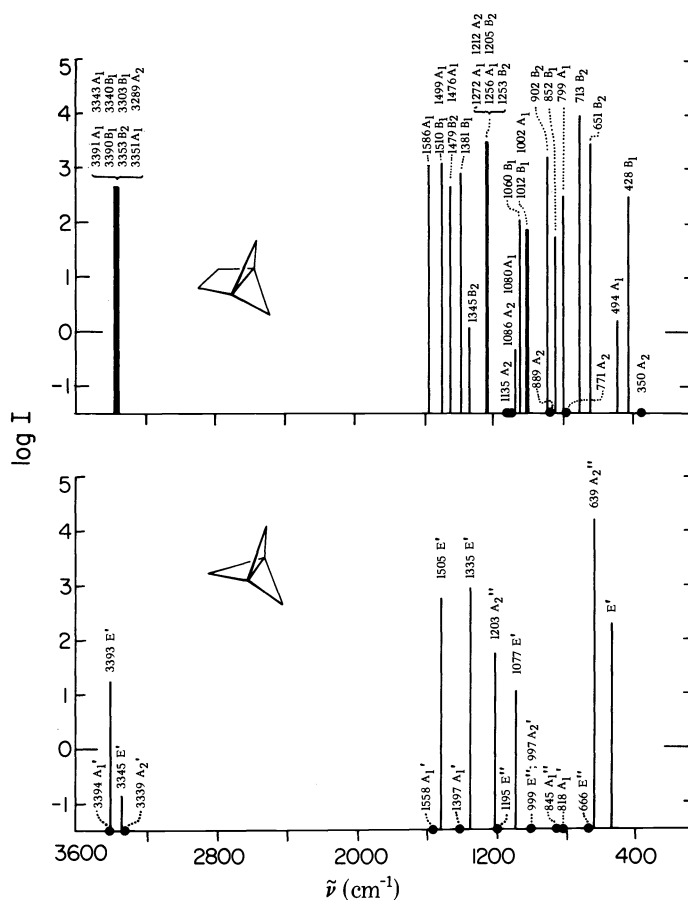


Fig. 2

Fig. 2. Calculated (MNDO) infrared spectra of the propellanes **2** and **3**. Note the logarithmic scale for intensities.

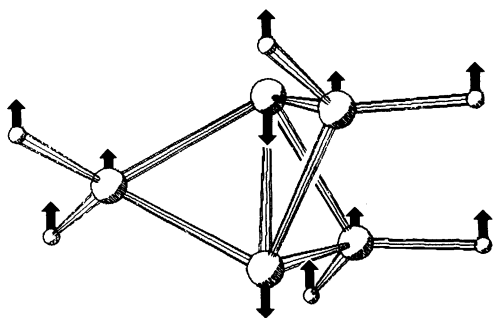


Fig. 3

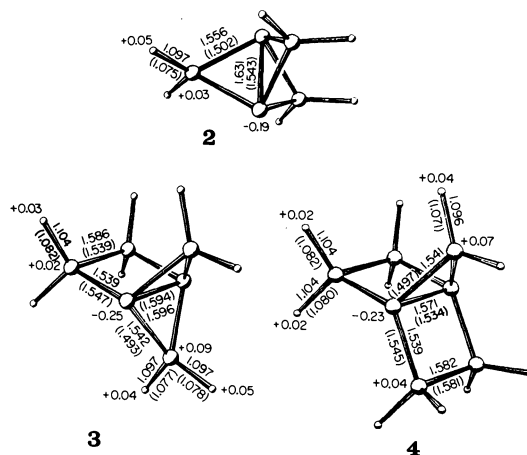


Fig. 4

Fig. 3. Atom displacements in the "bobbing" mode of [1.1.1]propellane **2** calculated by the MNDO method (calc. 639 cm^{-1} , obs. 603 cm^{-1}).

Fig. 4. Optimized bond lengths in propellanes (MNDO, and in parentheses 6-31G* SCF for **2** and **3** and 4-31G for **4**) and atomic charges (MNDO).

ADAMANTENE

Bridgehead olefins contain *trans*-cycloalkene structures. As the ring containing the *trans* juncture decreases in size, the strain imposed on the double bond increases and compounds containing a *trans*-cycloheptene or smaller ring are not stable at room temperature (2,3,13) unless they are protected by very bulky groups (14). Calculations (3,13,15) suggest that the severe distortion of the double bond in such bridgehead olefins is not a simple twist but rather, that the doubly bonded carbon next to the bridgehead pyramidalizes, i.e., rehybridizes towards sp^3 . The electronic structure of such severely distorted double bonds is of considerable interest. We have already reported the preparation of matrix-isolated adamantene **7**, containing a *trans*-cyclohexene ring, by gas-phase dehalogenation of 1,2-dihalo-genated adamantanes with metal vapor (16). We have since improved this technique and obtained better ir spectra of **7**, and of **7** singly deuterated in the vinylic position. We have now also prepared the same matrix-isolated species from the known (17) diazo precursor **8**, thus providing a further proof of the structural assignment (Fig. 5). The latter procedure makes the measurement of the uv absorption spectrum far easier since there is no interference from excess metal atoms.

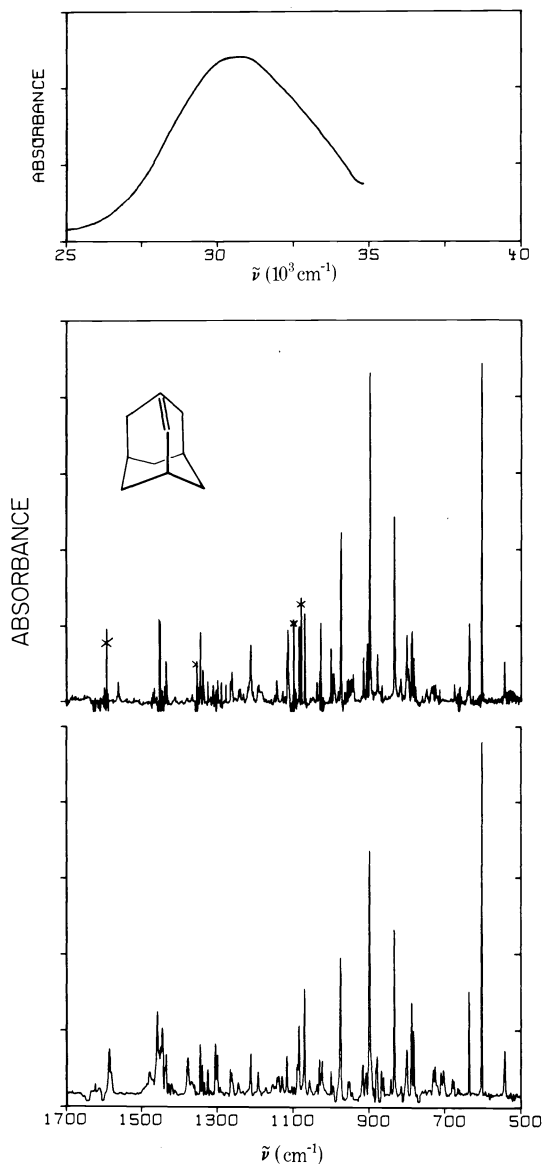


Fig. 5. Uv (top) and ir (bottom) absorption spectrum of adamantene (**7**) produced by irradiation of **8** in a nitrogen matrix at 14K. In the center, the ir spectrum of **7** obtained by dehalogenation of 1,2-diiodoadamantene with microwave-discharged sonicated potassium vapor in argon. Argon matrix, 14K. Impurity peaks are crossed.

The size of **7** has so far precluded a complete vibrational analysis but several features of the ir spectra are of interest. The C=C stretch is most likely associated with a weak band at 1586 cm^{-1} . A definitive assignment is awaiting the completion of our polarization, deuteration, and Raman studies, but when it is considered that increasing distortion should weaken the π bond, the value compares reasonably with the "standard" trisubstituted ethylene value of $1667\text{--}1678\text{ cm}^{-1}$ (18) and with the value 1610 cm^{-1} reported (13) for homo-adamantene (**9**), which contains the less strained *trans*-cycloheptene ring. The value found for **7** is still far above that considered usual for the C-C single bond stretch, indicating that the π bond, though weakened, has substantial strength. No vinylic C-H stretch is observed in **7** above the aliphatic C-H stretches; the vinylic C-D stretch is observed at 2196 cm^{-1} . If we assume that the ratio of the C-H and C-D stretching frequencies is 1.35 as in **9** [3000 cm^{-1} , 2218 cm^{-1} (13)], the vinylic C-H stretch of **7** would be expected at $\sim 2970\text{ cm}^{-1}$ where it would indeed be buried under the aliphatic C-H stretches. This continues the trend from the usual region, $3020\text{--}3040\text{ cm}^{-1}$ (18) towards lower vinylic C-H stretching frequencies for heavily distorted double bonds, which is noticeable already for **9**. The trend is in accordance with the notion that the severe distortion causes the vinylic carbon to pyramidalize. The out-of-plane bend of the vinylic hydrogen of **7** occurs at 900 cm^{-1} and was assigned by reference to the deuterated analog, where it lies at 632 cm^{-1} . The value of the out-of-plane C-H bend in **9** is 848 cm^{-1} (13) and the usual region for trisubstituted ethylenes is $800\text{--}830\text{ cm}^{-1}$. Also this decreasing trend is nicely compatible with the notion that the growing strain induces a gradual change in the hybridization of the vinylic carbon towards sp^3 .

The presence of an intense uv transition at $\sim 31\,500\text{ cm}^{-1}$, which we assign as $\pi\pi^*$, is perfectly compatible with the presence of a severe distortion of the C=C bond, which should raise the HOMO energy and lower the LUMO energy. We have attempted to calculate a rough estimate of the excitation energy as follows. The geometry of **7** was first optimized at the MNDO level. The lowest singlet excitation energy was then calculated for ethylene at its ordinary geometry and at a geometry distorted into the calculated shape of the double bond of **7**, using large-scale configuration interaction (4000 configurations) on the triplet orbitals in a double zeta basis set with polarization (19). The lowering of the first excitation energy of ethylene upon distortion into the requisite shape estimated in this fashion was then applied to the standard energy of the $\pi\pi^*$ transition of planar trialkylethylenes: the result was about $40\,000\text{ cm}^{-1}$, in fair agreement with the observed value.

AZAHOMOADAMANTENE

Severe twisting of a bridgehead C=N double bond is quite analogous to that of the C=C bond, except that now, there is no vinylic hydrogen and a new low-energy electronic state appears ($n\pi^*$). Figure 6 shows the spectra of azahomoadamantene **10**, a compound with a severely distorted bridgehead C=N double bond. It has been prepared in matrix isolation by the irradiation of 1-adamantyl azide in a reaction in which it was already previously postulated as an intermediate at ordinary temperatures (20, cf. 21). It dimerizes upon warmup similarly as **7** and **9** to yield the known (20)dimer. Extended irradiation converts **10** to the known (22) stable isomer **11**. The ir and Raman spectra of **10** contain only one very characteristic vibration, the C=N stretch, which appears as a pair of lines at 1602 and 1607 cm^{-1} . The shift to lower frequencies from the region of $1650\text{--}1660\text{ cm}^{-1}$ considered

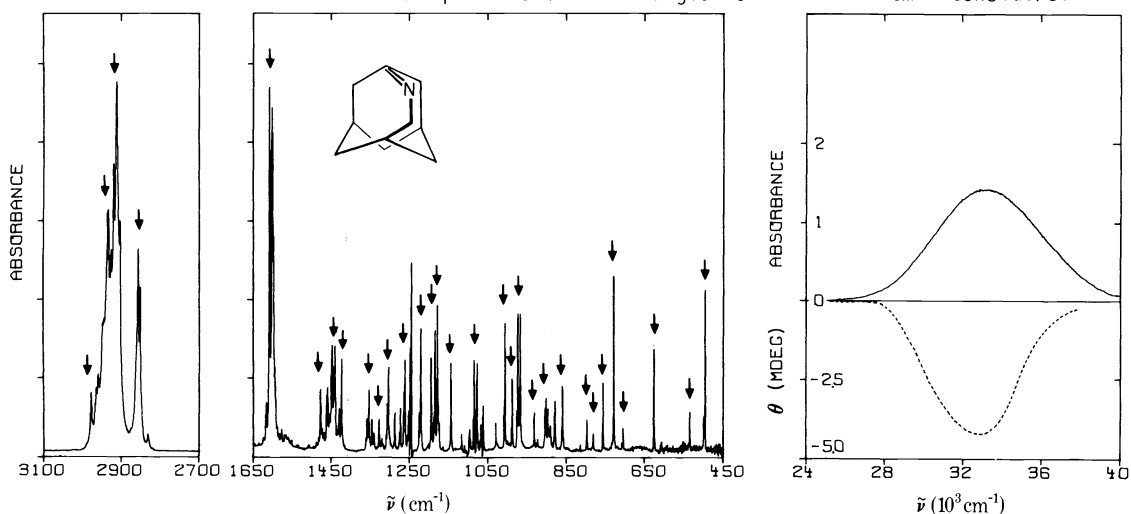


Fig. 6. Left: infrared and right: uv (full) and cd (dotted) spectra of azahomoadamantene (**10**) in nitrogen matrix at 14K. The arrows indicate peaks which are also observed in the Raman spectrum.

normal for trialkyl substituted C=N bonds (23) is entirely analogous to the shift of the C=C stretch observed in **9** (13) and shows a similar weakening of the two kinds of double bonds upon torsion (cf. 1650 cm^{-1} for **11**).

The first band in the uv absorption spectrum of **10** lies at $\sim 33\,000\text{ cm}^{-1}$ and is thus significantly red-shifted relative to that of unstrained alkyketimines ($\sim 43\,000\text{ cm}^{-1}$). The most likely assignment is $n\pi^*$, in agreement with *ab initio* SCF-CI calculations on $\text{CH}_2=\text{NH}$ mentioned below.

The suspected absence of a symmetry plane in **10** (not obvious from the formula drawn) and the presence of a double minimum have been confirmed by a matrix photoresolution experiment. Irradiation of the sample with circularly polarized light at the wavelengths of the first absorption band induces optical activity which satisfies all the usual tests for authentic circular dichroism and shows that **10** is chiral. The cd spectrum is shown in Fig. 6. As expected, it reverses its sign when the handedness of the circularly polarized light used for the photoresolution is reversed; we do not presently have an absolute assignment of chirality.

The mechanism of the photoresolution is suggested by calculations using large-scale configuration interaction similarly as for **7** (19): Fig. 7 shows the resulting potential energy diagram for the twisting of the double bond of $\text{CH}_2=\text{NH}$ from 0 to 90 degrees. In this process, the ground state is calculated to increase in energy by about 60 kcal/mol, while the $n\pi^*$ excited state decreases by about 45 kcal/mol. Thus, the C=N twist imposed by the ring system lowers the excitation energy. Taking Fig. 7 as a rough guide, the observed red shift of about $10\,000\text{ cm}^{-1}$ in **10** relative to planar alkyketimines corresponds to a twist angle of about 35° . Absorption into the $n\pi^*$ state will be followed by a rapid relaxation to the minimum at 90° twist. Return to the ground state at this geometry will be rapid and relaxation will occur both towards twist angles larger and smaller than 90° , i.e., into both enantiomers. Since circularly polarized light is absorbed more strongly by one than the other, in the photostationary state **10** will be partially photoresolved (24).

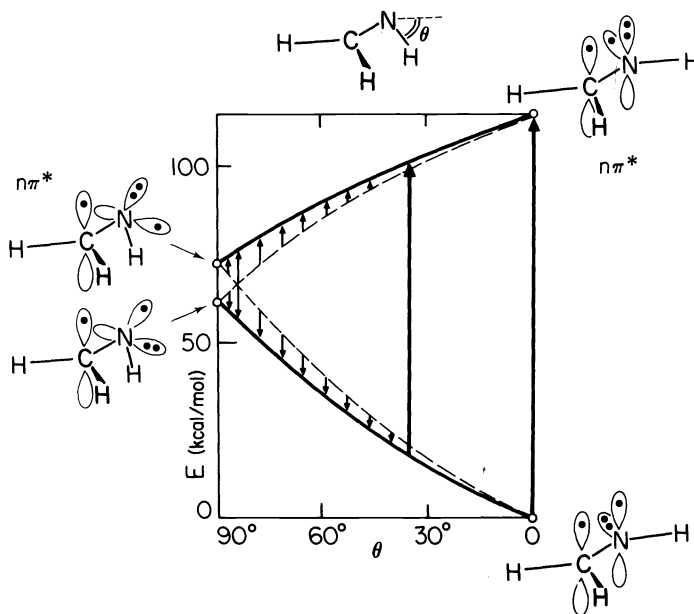


Fig. 7. Calculated (SCF-CI) energy of the lowest two singlet states of $\text{CH}_2=\text{NH}$ as a function of the twisting angle.

CONCLUSION

Direct observation of molecules with highly strained single and double bonds provides information about their molecular and electronic structure. Experiments on the compounds mentioned here continue and it is hoped that more will be learned about these unusual species.

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REFERENCES

1. D. Ginsburg, Propellanes, Verlag-Chemie, Weinheim, West Germany (1975), pp 30-53, and references therein; D. Ginsburg, Propellanes: Sequel I, Technion-Israel Institute of Technology, Haifa, Israel (1981).
2. A. Greenberg and J.F. Liebman, Strained Organic Molecules, Academic Press, New York (1978).
3. O. Ermer, Aspekte von Kraftfeldrechnungen, Wolfgang Baur Verlag, Munich, West Germany (1981).
4. K.B. Wiberg and F.H. Walker, submitted for publication.
5. K.B. Wiberg, F.H. Walker, W.E. Pratt, and J. Michl, unpublished results.
6. F.H. Walker, K.B. Wiberg, and J. Michl, J. Am. Chem. Soc. **104**, 2056 (1982).
7. K.B. Wiberg and G.J. Burgmaier, Tetrahedron Lett. **317** (1969); P.G. Gassman, A. Topp, and J.W. Keller, ibid. **1093** (1969); K.B. Wiberg and G.J. Burgmaier, J. Am. Chem. Soc. **94**, 7396 (1972); D.H. Aue and R.N. Reynolds, J. Org. Chem. **39**, 2315 (1974); K.B. Wiberg, W.E. Pratt, and W.F. Bailey, J. Am. Chem. Soc. **99**, 2297 (1977).
8. P.G. Gassman and G.S. Proehl, J. Am. Chem. Soc. **102**, 6862 (1980); K. Mlinaric-Majerski and Z. Majerski, J. Am. Chem. Soc. **102**, 1418 (1980).
9. D.P.G. Hamon and V.C. Trenerry, J. Am. Chem. Soc. **103**, 4962 (1981); U. Szeimies-Seebach, J. Harnish, G. Szeimies, M.V. Meerssche, G. Germain, and J.P. Declercq, Angew. Chem. Int. Ed. Engl. **17**, 848 (1978); U. Szeimies-Seebach and G. Szeimies, J. Am. Chem. Soc. **100**, 3966 (1978).
10. P.E. Eaton and G.H. Temme, J. Am. Chem. Soc. **95**, 7508 (1973).
11. K.B. Wiberg and J.J. Wendoloski, J. Am. Chem. Soc., in press (1982).
12. M.J.S. Dewar, G.P. Ford, M.L. McKee, H.S. Rzepa, W. Thiel, and Y. Yamaguchi, J. Mol. Structure **43**, 135 (1978).
13. D.J. Martella, M. Jones, Jr., P.v.R. Schleyer, and W.F. Maier, J. Am. Chem. Soc. **101**, 7634 (1979).
14. M. Jones, personal communication.
15. N.L. Allinger and J.T. Sprague, J. Am. Chem. Soc. **94**, 5734 (1972).
16. R.T. Conlin, R.D. Miller, and J. Michl, J. Am. Chem. Soc. **101**, 7637 (1979).
17. D.J. Martella, M. Jones, Jr., and P.v.R. Schleyer, J. Am. Chem. Soc. **100**, 2896 (1978).
18. D.G. Rea, Anal. Chem. **32**, 1638 (1960).
19. The method of calculation was described earlier: V. Bonačić-Koutecký, R.J. Buenker, and S.D. Peyerimhoff, J. Am. Chem. Soc. **101**, 6917 (1979).
20. H. Quast and P. Eckert, Justus Liebigs Ann. Chem. **1727** (1974).
21. E.P. Kyba and R.A. Abramovitch, J. Am. Chem. Soc. **102**, 735 (1980).
22. T. Sasaki, S. Eguchi, and N. Toi, J. Org. Chem. **44**, 3711 (1979); Heterocycles **7**, 315 (1977).
23. K.A.W. Parry, P.J. Robinson, P.J. Sainsbury, and M.J. Waller, J. Chem. Soc. B **700** (1970).
24. The principle of photoresolution by this type of mechanism has been demonstrated earlier at ordinary temperatures: N.A.P. Kane-Maguire and C.H. Langford, Can. J. Chem. **50**, 3381 (1972).