rotation takes place from cis to trans indicating that the barrier is not solely determined by the electron density in the $O(p_x, p_y)$ orbitals. For O_2F_2 the highest two occupied molecular orbitals are O–O antibonding, the trans pair being slightly more antibonding than the cis pair. This may account for the higher trans barrier. These orbitals are less O–O antibonding at a dihedral angle of 90° than at either 0° or 180°.

Conclusions

The cis and trans barriers in O_2F_2 are calculated to be 16.62 and 20.83 kcal mole^{-1}, respectively, with a dipole moment of 0.80 D and an equilibrium dihedral angle of 85°. The cis barrier in H_2O_2 is found to be 5.33 kcal mole^{-1} in the same approximation. A gross orbital population analysis shows that the behavior of the $O(p_x, p_z)$ electron density as a function of dihedral angle is similar to the behavior of the total energy as a function of dihedral angle. The opposite effect is true for H_2O_2.

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A spectroscopic investigation of diazomethane isomers

Few small molecules have such an abundance of known or suspected structural isomers as diazomethane (structure I in Fig 1). Both the cyclic isomer
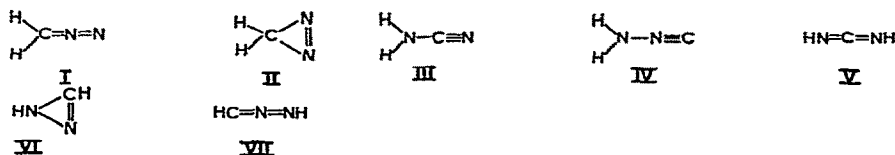

Fig. 1. Structures of diazomethane and its isomers.

diazirine (II) and cyanamide (III) are themselves and their alkyl derivatives well known and characterised. Alkyl derivatives of isocyanamide (IV) and carbodiimide (V) have been prepared, but no evidence of isodiazirine (VI) is believed to exist. There has been some consideration of isodiazomethane (VII) in connection with various unexplained chemical and physical observations (vide infra), but further arrangements of the five atoms constituting diazomethane defy plausibility on valence grounds.

As part of an attempt to establish the identity of a carrier or carriers of a few vibrational absorptions produced during the photolysis of diazomethane in solid argon at 4° K[1], some spectroscopic experiments were carried out during a brief sojourn in Tübingen to determine whether isodiazomethane was responsible for the observed effects. Earlier chemical evidence[2-4] had been interpreted to signify that this was a product of a reaction in which a labile hydrogen atom of diazomethane was transferred to the opposite end of the heavy-atom skeleton. The best spectrum (of three independent successful trials) is presented in Fig. 2. In the preparation of this sample, drying the contents of a flask (refrigerated at 242° K) with phosphorus pentoxide and pumping for twelve hours (with oil diffusion pump and liquid-nitrogen trap interposed) removed water and diethyl ether respectively. The more volatile fractions from the flask were distilled during seven hours onto the caesium bromide window of a liquid-nitrogen optical cryostat[5] via glass tubing. The source flask contained the products of a hydrolysis reaction of diazomethyllithium[6]; following the removal of solvent, the oily residue gradually became intensely red and increasingly viscous, indicative of polymerisation or other decomposition processes. The films distilled onto the cryostat window were always colourless to visual inspection, indicating extinction coefficients less than $20 \ 1 \ \text{mole}^{-1} \ \text{cm}^{-1}$ in the visible region, but uv spectrophotometric measurements of the frozen film were impracticable.

By comparison of Fig. 2 with the known spectrum of solid diazomethane[7] one can assign the absorptions at 464, 555, 563, 572, 1400, 2092, 3043, and 3151
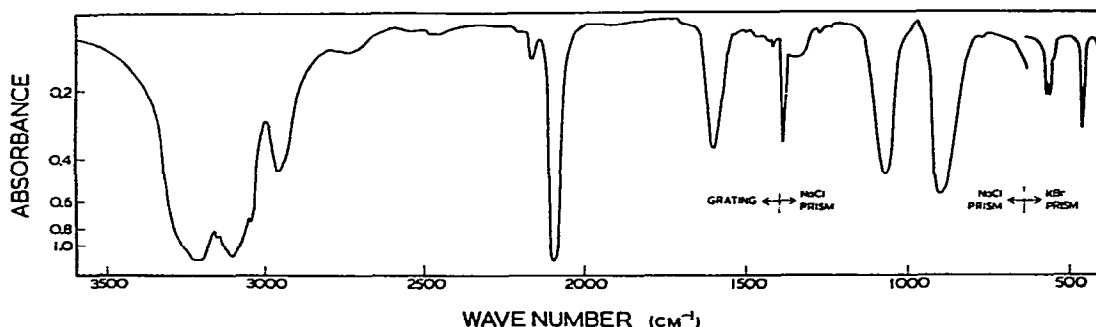

Fig. 2. IR absorption of solid film at 77° K of product of "isodiazomethane" preparation (Perkin-Elmer 221 spectrometer; spectral slit width, 2–5 cm⁻¹).

cm^{-1} (corrected wave numbers) to this substance. Traces of water caused broad absorptions near 1675 and 3400 cm^{-1}. The intense but variable (in the different trials) feature at 2953 cm^{-1} can indicate a methyl group absorption, but the carriers of this band, and those at 1365, 1469, and 2737 cm^{-1} cannot be positively identified at this time. The remaining significant absorptions at 898, 1074, 1606, 2159, 3105 and 3220 cm^{-1} are, by the constancy of their intensity ratios, attributed to one carrier. Although in one trial the 2159 cm^{-1} feature seemed to have a relatively diminished absorbance, further recent measurements[8] of ethereal solutions near 300° K have demonstrated that the 2159 cm^{-1} absorption is properly placed with the others above. On the basis of these solution experiments, and of others with deuterated products, isocyanamide (IV) has been proposed[8] as the carrier. The solution spectrum can be assigned as follows: 3290 and 3172 cm^{-1}, v(N–H) fundamentals, which shift to 2420 and 2330 cm^{-1} (calc.[9]: 2432 and 2345 cm^{-1}) for the deuterated product; 2140 cm^{-1}, v(C≡N) mode, found at 2130 cm^{-1} for the deuterated product; 1630 cm^{-1}, NH_2 deformation mode. There was no absorption in the 1600 cm^{-1} region for the deuterated product, but the 1200 cm^{-1} region was opaque because of solvent absorption. However the overtone of the deformation vibration at 2470 cm^{-1} was observed, its intensity enhanced probably through Fermi resonance interaction with the stretching fundamentals.

The absorptions of the frozen film can be facilely correlated with the solution spectrum above 1600 cm^{-1}, the difference being readily attributed to small solvent shifts in the ether and moderately extensive hydrogen bonding in the solid. Furthermore, the additional absorptions detected in the solid can be assigned as follows: 898 cm^{-1}, NH_2 rocking mode; and 1074 cm^{-1}, the v(N–N) mode. Some absorptions below 600 cm^{-1} might also be due to isocyanamide as the observed features do not correlate exactly with those of solid diazomethane[7], but the differences are slight; unfortunately the KBr prism was used in only one experiment, so intensity ratio data are not available. However the 898 and 1074 cm^{-1} bands observed in the solid film provide confirmation of isocyanamide as the carrier by comparison with the fundamentals of cyanamide[10], which indicates that the assignments are indeed reasonable. Furthermore an experimental estimate (10^{-3} torr) of the vapour pressure of isocyanamide at 238° K is of the order of magnitude extrapolated for cyanamide[10]; hydrogen bonding is cited as the cause of the small magnitude in both cases.

In the diazomethane photolysis experiments[1] a mysterious absorption at 2169 cm^{-1} was detected. As the more intense (in the solid) isocyanamide bands were not detected, the 2169 cm^{-1} feature could not be assigned to this substance. In fact, the 2169 cm^{-1} absorption, and its 2146 cm^{-1} counterpart for deuterated starting materials, were tentatively attributed to isodiazomethane. Of the seven structural isomers depicted in Fig. 1, all but V and VII can be readily eliminated from consideration. A doubling of the vibration-rotational fine structure, the relative intensities of the two sets of lines varying from preparation to preparation

at similar temperatures, has been noted[11] in the 2150 cm^{-1} region when gaseous diazomethane at a total pressure of 2.5 torr was investigated. The authors suggested that 'isodiazomethane', referring to the earlier organic studies[2,3], might have been responsible but this has since been shown to be isocyanamide instead. Therefore, that the vapour pressure of the latter was sufficient to produce the observed effects is doubtful since other (more) intense fundamentals ought to have been detected as well. In the argon matrix experiments[1], the absence of other absorptions having appropriate intensity behaviour in various experiments is taken to suggest that the 2169 cm^{-1} absorption is the most intense fundamental of its carrier. The tentative proposal[1] of HCNNH as the carrier of both gas and matrix spectra is not unequivocably affected by the conclusions of the isocyanamide experiments.

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A semiempirical SCF-CI study of steric effects in aza derivatives of biphenyl in relation to their electronic spectra

Introduction

The twist of the co-annular bond caused by steric effects in a biphenyl-type molecule affects the electronic absorption spectrum of this compound. Since the interaction of the π orbitals across the bond and hence the conjugation of the system are maximal when the system is planar any deviation from planarity