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Cyclopentadienylidene. A Matrix Isolation Study Exploiting Photolysis with Unpolarized and Plane-Polarized Light

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Abstract: Diazocyclopentadiene (**1**) was photolyzed in N_2, CO, and other low-temperature matrices. The resulting carbene, cyclopentadienylidene (**2**), was characterized by its UV and IR spectra, and its thermal dimerization and reaction with CO were observed. Photolysis of **1** with plane-polarized light gave matrices exhibiting linear dichroism. Comparison of dichroic IR and UV spectra revealed that the photolysis proceeds via an excited A_1 state of the diazo compound. Plane-polarized irradiation of the corresponding ketene (**4**) in CO matrices resulted in photoreorientation of the molecules of **4** without significant loss.

Introduction

When diazocyclopentadiene (CpN_2, **1**) is photolyzed in a solid medium, such as hexafluorobenzene or hexachlorobutadiene at 77 or 4 K, a triplet ESR spectrum can be observed, which is attributed to the ground state of cyclopentadienylidene (**2**).[2] Analysis of the ESR spectrum reveals that one unpaired electron is in the π system and the other is localized in an in-plane orbital at C-1. An EHT MO calculation[3] accords with this view of a triplet ground state, in predicting that the energies of the in-plane orbital at C-1 and the delocalized π orbital should lie close together (within 0.13 eV).

Nevertheless, the solution photochemistry of CpN_2 seems to proceed largely by reaction of a singlet excited state of cyclopentadienylidene. Thus, the observed C–H insertion reactions of **2** and its virtually stereospecific additions to alkenes are usually interpreted on the basis of a singlet rather than a triplet carbene.[4–7] It is likely, therefore, that photolysis of CpN_2 first produces singlet **2**, which in solution undergoes reaction faster than intersystem crossing.

Because of the high reactivity of the singlet, little evidence has been obtained for processes involving the triplet ground state of **2**. An attempt to observe the UV absorption spectrum of ground-state **2** in low-temperature matrices has been reported,[8] but the high concentrations employed and the rather unfavorable absorption patterns of the various species (vide infra) prevented detection of **2**, and only the carbene dimer, fulvalene (**3**), was observed. In this paper, we report the results of a matrix IR and UV study of ground-state **2** and its thermal dimerization and reaction with CO.[9] The matrix reaction of **2** with O_2 has also been reported recently.[10]

Experimental Section

Matrix experiments were performed at 12–20 K using an Air Products Displex CS-202 closed-cycle helium refrigerator. Details of the apparatus have been published previously.[11] IR spectra were recorded on a Grubb Parsons Spectromajor spectrophotometer, and all IR spectra were run with a polished germanium filter in the beam to remove visible radiation. Polarized IR spectra were obtained by means of a SpecAc aluminum grid polarizer on a KRS-5 substrate. UV spectra were run on a Perkin-Elmer 356 spectrophotometer, with the use of a Polacoat 105 UV WMR polarizer on a quartz substrate in polarization experiments.

Table I. IR Bands of CpN_2 (1) and CpCO (4) in CO Matrices

CpN_2 (1)		CpCO (4)	
$\bar{\nu}$ (cm^{-1})	symmetry[a]	$\bar{\nu}$ (cm^{-1})	symmetry[a]
2104 (vs)[b]	A_1[c]	2133 (vs)	A_1[c]
2096 (s)	A_1	2130 (s)	A_1
		2082 (w)	
		2079 (w)	
1583 (w)		1444 (w)	
1421 (m)	A_1	1432 (m)	A_1
1413 (m)	A_1	1396 (w)	
1389 (m)	A_1	1385 (w)	
		1380 (w)	
		1326 (w)	
1297 (m)	A_1		
1275 (w)			
1228 (w)			
1075 (w)		1080 (w)	
1064 (m)	A_1		
926 (w)		927 (w)	
915 (m)	A_1	901 (m)	A_1
725[d] (s)	B_1 or B_2	737 (m)	B_1 or B_2
687 (w)		699 (w)	
652 (w)		640 (w)	
626 (w)			
568 (w)	B_1 or B_2	582 (m)	
		527 (w)	

[a] Determined in polarization experiments. [b] Qualitative intensities: w = weak, m = medium, s = strong, vs = very strong. [c] The A_1 modes of both molecules are split into two components by matrix effects. [d] This band is at 713 cm^{-1} in N_2 matrices.

Table II. IR Bands ($\bar{\nu}$, cm^{-1}) of Cyclopentadienylidene (2) in N_2 at 20 K

1345 (w)[a]	922 (w)
1335 (m)	703 (s)
1101 (w)	577 (w)
1074 (w)	

[a] Qualitative intensities: w = weak, m = medium, s = strong.

The photolysis source was a 125-W medium-pressure Hg arc, either focused with $f/4$ quartz optics on the entrance slit of an Applied Photophysics M300 High Radiance monochromator, or unfocused and filtered with a 4-cm quartz water cell when high-intensity illumination was required. Polarized irradiations were carried out with monochromated light passed through a Polacoat 105 UV WMR polarizer.

All matrix gases were "Grade X" gases supplied by BOC Ltd. Matrix mixtures were prepared and matrix ratios (MR) determined using conventional vacuum line techniques, and matrices were deposited on a CsBr window at 20 K using the pulsed matrix isolation technique.[12] Diazo-

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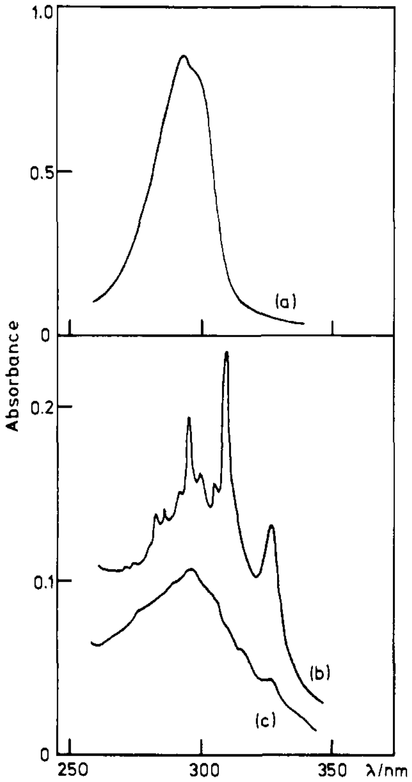

Figure 1. UV absorption spectra, N_2 matrices at 20 K: (a) CpN_2, MR 10^3; (b) CpN_2 after complete photolysis (λ >300 nm), MR 10^3; (c) CpN_2 after complete photolysis (λ >300 nm), MR 1.5×10^6.

cyclopentadiene[13] (**1**) and *o*-diazoquinone[14a] (**5**) were prepared by published methods.

Results

CpN_2 in N_2 and Ne Matrices. CpN_2 in N_2 matrices had UV absorptions at 293 (λ_{max}) and 300 nm (shoulder) (Figure 1a). The spectrum did not alter significantly over a 1500-fold concentration range (MR 10^3–1.5×10^6) or on change of matrix host from N_2 to CH_4, Ne (4 K), or CO. IR spectra of CpN_2 in both N_2 and CO matrices were very similar, showing strong ν_{CNN} bands at 2100 cm^{-1} and series of weaker bands (Table I). Monitoring the photolysis of CpN_2 at 12 K in N_2 matrices by UV and IR spectroscopy has led to the following observations.

1. UV irradiation (λ >300 nm) of CpN_2 caused the disappearance of its IR bands. At moderate concentration (MR 10^3), the resulting matrix had a UV spectrum (Figure 1b) exhibiting the characteristic sharp absorptions of fulvalene (Cp_2, **3**).[8] At low concentration (MR 10^4–1.5×10^6), however, the spectrum of Cp_2 was much weaker, and the principal absorption (Figure 1c) was a broad band with λ_{max} 296 nm. This band was too intense to belong to residual CpN_2, as judged from the disappearance of the IR bands of this species, and we assign it, therefore, to cyclopentadienylidene (Cp:, **2**).

2. A series of IR bands, arising simultaneously with the disappearance of the absorptions of CpN_2, as also assigned to Cp: (Table II).

3. When the photolysis was carried out in a matrix of 95 atom % $^{15}N_2$, no IR bands due to $Cp^{15}N_2$ were seen. The loss of N_2 is therefore irreversible.

4. When matrices containing the carbene Cp: but little or no residual CpN_2 were annealed, the resulting UV spectra clearly indicated the formation of fulvalene (Cp_2) (cf. Figures 1b and 1c). The same process was accompanied by a diminution of the IR bands of Cp: and the appearance of two groups of bands at 1360 and 765 cm^{-1} and a single band at 700 cm,$^{-1}$ which we thus assign to Cp_2 (Figures 2a and 2b). As estimated from the IR band intensities of Cp:, however, the extent of the conversion of Cp: into Cp_2, in several experiments, never exceeded about 20%.

5. Prolonged irradiation of Cp: at 12 K with the full Hg arc (water filter only) caused bleaching of the UV absorption at λ_{max} 296 nm, diminution of the IR bands of Cp:, and the appearance of new IR bands at 3315 (several), 2974, 985, 796, 656 (several), 615 (several), 546, and 513 cm^{-1} (Figures 2a and 2c). The bands at 3315 cm^{-1} suggest a terminal alkyne, but the observed spectrum is not consistent with formation of either ethyne[15] or 1,4-pentadiyne,[16] a sample of which was also isolated in N_2 at 12 K.

6. A single experiment with a Ne matrix at 4 K (MR 10^4) was conducted. After disappearance of CpN_2, the resulting UV spectrum showed that the initial formation of Cp_2 was favored more in Ne at 4 K than in N_2 at 12 K, but the IR spectrum also showed the presence of Cp: by its 703-cm^{-1} band. Further photolysis with the full Hg arc (water filter only) led to the disappearance of this IR band and bleaching of the 296-nm UV absorption of Cp:, the latter being observable only as a pronounced flattening of the base line beneath the fulvalene spectrum.

CpN_2 in CO, CO-Doped N_2, and CH_4 Matrices. When CpN_2 was photolyzed in CO at 20 K (MR 10^3), neither the carbene (Cp:) nor fulvalene (Cp_2) was observed. Instead, as the IR bands of CpN_2 diminished, there arose new bands at 2133, 2130 (ν_{CCO}, vs), 2082, and 2079 cm^{-1} ($\nu_{C^{13}CO}$, vw), indicating the formation of a ketene, and a series of bands at lower frequencies (Table I). Figure 3 shows the corresponding transformation of the UV spectrum that accompanied this reaction.

The ketene was assigned the structure CpCO (**4**) on the following basis.

1. Its IR spectrum closely resembled that of CpN_2 in the region 1600–400 cm,$^{-1}$ both in position and intensity of bands and also in the determined band symmetries (vide infra) (Table I).

2. Photolysis of CpN_2 in N_2 matrices doped with CO (1–20%) resulted in formation of both Cp: and CpCO. As expected, the CpCO/Cp: ratio increased with increasing CO content. On subsequent annealing, both UV and IR absorptions of Cp: diminished, and those of CpCO grew further, indicating a thermal reaction between Cp: and CO (Figure 4).

3. *o*-Diazaquinone (**5**),[14] although somewhat unstable and not very volatile, could nevertheless be isolated in N_2 at 12 K by direct sublimation from a side tube at room temperature, with simultaneous condensation of N_2. The optical quality of the matrices obtained in this way was unfortunately consistently poor so that UV spectra suffered from severe background slope and poor resolution. IR spectra were not so badly affected, however, and irradiation (λ >300 nm) of **5** led to disappearance of its IR bands (ν_{max} 2130, 1640, and 1620 cm^{-1}) and appearance of the UV spectrum of CpCO.

The ketene (CpCO) itself was much more resistant to photolysis than CpN_2. Irradiation (λ 254 ± 10 nm) of CpCO in CO-doped N_2 (various concentrations) failed to produce any convincing degree of reversal to Cp: and CO. Similar results were also obtained with CpCO in CO-doped Ar matrices.

In contrast to CO, CH_4 did not react with the carbene (Cp:). Photolysis (full-arc) of CpN_2 in CH_4 (MR 10^3) at 20 K was monitored by UV spectroscopy, which showed the formation of fulvalene (Cp_2). The carbene was therefore not intercepted by a rapid reaction with the host molecules.

Irradiation of CpN_2 with Plane-Polarized Light. Several papers have recently appeared describing experiments on the irradiation of matrix-isolated molecules with plane-polarized light[17] These have demonstrated that, in suitable cases, polarized photolysis of trapped species produces samples with molecules having net orientation, and with linearly dichroic UV and IR spectra. The

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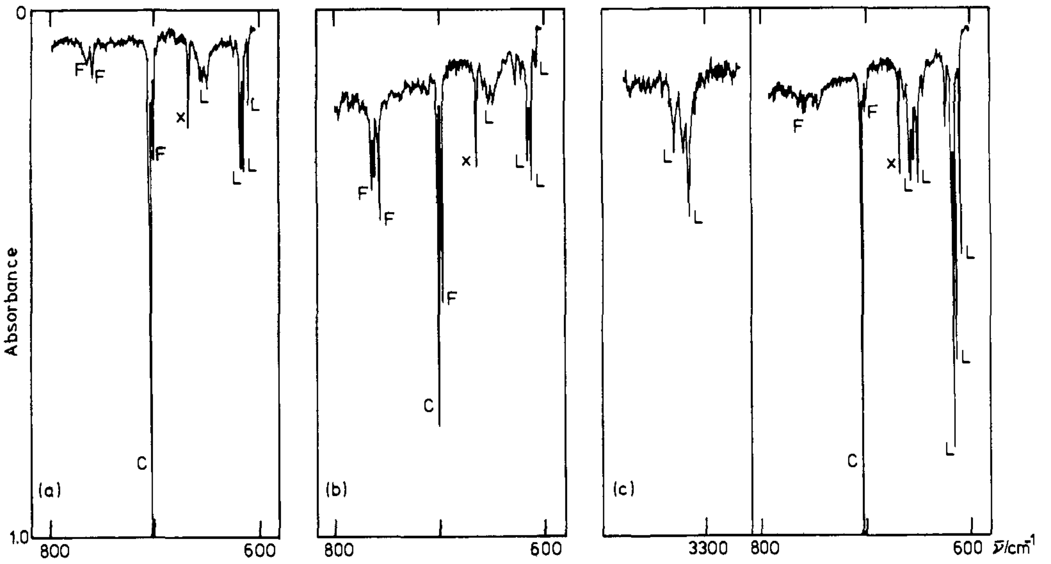

Figure 2. IR spectra, N_2 matrices at 12 K: (a) CpN_2 after 15-min, irradiation (λ >310 nm), MR 2 × 10^3; (b) same sample after annealing at 30 K; (c) CpN_2 after 34-min irradiation (λ >285 nm), then 80 min (λ >200 nm), MR 10^4. Band assignments: C (Cp:), F (Cp_2), L (**6**), × (CO_2 impurity).

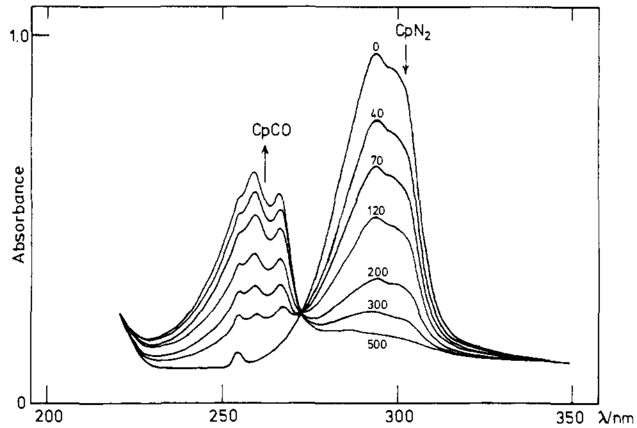

Figure 3. UV absorption spectra showing the progress of photolysis (λ >300 nm) of CpN_2 in CO at 12 K, MR 10^3. Photolysis times (seconds) are indicated. An impurity in the cold CsBr window gives rise to an absorption with λ_{max} 254 nm; this is present throughout and appears also in Figures 5 and 7.

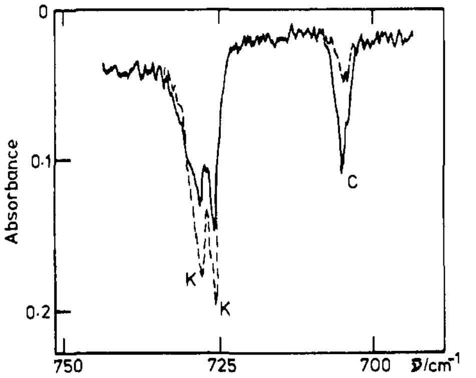

Figure 4. IR spectra, N_2 matrix doped with 10% CO (12 K): (—) CpN_2 after 9-min photolysis (λ >300 nm), MR 10^4; (---) same sample after annealing at 24 K. Band assignments: C (Cp), K (CpCO).

results have been exploited to yield information on the properties of both the trapped molecules themselves and the matrix host.

The three molecules (CpN_2, CpCO, and the carbene Cp:) all belong to the same point group (C_{2v}). Symmetry-allowed vibrational and electronic transitions for these species have transition moments parallel to the C_2 axis (A_1) or perpendicular to it (B_1 out-of-plane, B_2 in-plane). Thus for a molecule fixed rigidly in a matrix and interacting with plane-polarized radiation of appropriate frequency, the probability of absorption will have a $\cos^2$ dependence on the angle between the transition moment vector of the molecule and the E vector of the radiation. A molecule for which this angle is small will have a much higher probability of absorbing a photon than a similar molecule for which this angle approaches 90°.

Figure 5 shows linear dichroism in the UV spectra of residual CpN_2 and product CpCO in CO at 12 K, following plane-polarized irradiation (λ 315 ± 10 nm) in the photochemically active absorption band of CpN_2. Although the absorption maximum of CpN_2 is at 290 nm, we chose to irradiate on the long-wavelength side of the band, 315 nm, to minimize the chances of secondary photolysis of the photoproduct CpCO. The degree of polarization $((A_\perp - A_\parallel)/(A_\perp + A_\parallel))$ for CpN_2 in Figure 5b is the largest so far reported for a matrix-isolated species. There is apparently some loss of molecular orientation during the conversion of CpN_2 into CpCO, because the latter shows less polarization than expected for molecules remaining spatially fixed throughout the reaction. Figure 6 shows part of the polarized IR spectra of CpN_2 in N_2 at 12 K after similar polarized irradiation. The band at 2100 cm^{-1} behaves in the same way as the UV absorption ($A_\perp > A_\parallel$), and since this band can be confidently assigned to the ν_{CNN} mode (A_1 symmetry), it follows that the photochemically active UV absorption is also of A_1 symmetry. On the other hand, the 703-cm^{-1} band, which is probably due to an out-of-plane C–H deformation, behaves in the opposite manner ($A_\parallel > A_\perp$). In this experiment it was impossible to differentiate bands of B_1 and B_2 symmetry, but the characterization of all but the weaker IR bands of CpN_2 as either A_1 or B_n (n = 1 or 2) was easily achieved (Table I).

A small degree of polarization of the carbene band at 703 cm^{-1} was observed during rapid scans of this region of the spectrum, immediately after irradiation. The sense of the polarization ($A_\perp > A_\parallel$) was consistent with some retention of molecular orientation during the ejection of N_2, but the magnitude was comparable to errors in reproducibility of the band intensities under the spectrometer conditions used, and the polarization did not survive long enough in the IR beam to allow slower and more precise scans to be made.

In contrast to the transient polarization of Cp:, the linear dichroism of matrix isolated CpN_2 was surprisingly persistent. At 12 K, the samples seems to be indefinitely stable, showing no reduction in degree of polarization over many hours, and in some cases several days. More remarkably, severe annealing, which caused evaporation of about half of the matrix, resulted in an overall loss of IR absorption intensity but no significant reduction in degree of polarization.

Irradiation of CpCO with Plane-Polarized Light. From Figure

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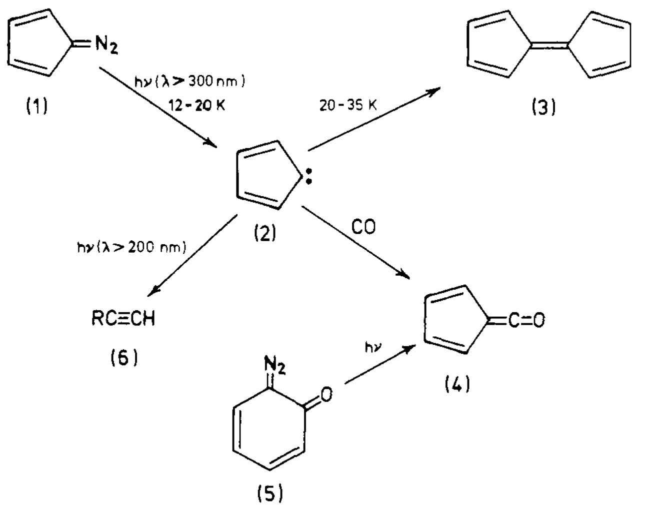
Scheme I



at 296 nm and the IR bands of Table II to the carbene Cp: (**2**) are based on the simultaneous appearance or disappearance of these features in four processes: (i) the photolysis of CpN_2, (ii) the dimerization of Cp:, (iii) the reaction of Cp: with CO, and (iv) the photolysis of Cp: to give an unidentified alkyne (**6**).

The ejection of N_2 from CpN_2 is apparently irreversible at these temperatures, since partial photolysis of CpN_2 in $^{15}N_2$ produced no detectable amount of $Cp^{15}N_2$, either immediately or on subsequent annealing. In contrast, photolysis of diazomethane in N_2 at 20 K results in exchange of nitrogen with the matrix host, presumably via methylene.[18] Hence there is a pronounced reactivity difference between these two carbenes.

The dimerization of Cp: to fulvalene occurs at 20–35 K in matrices containing little or no residual CpN_2. These conditions exclude the possibility of a reaction between Cp: and CpN_2. It has recently been pointed out that such carbene–carbene dimerizations, while energetically favorable, are exceedingly rare.[19] Ab initio calculations predict that there is no energy barrier on the potential surface describing the reaction of two methylenes to give ethene. The readiness with which the substituted methylene, Cp:, dimerizes at very low temperatures in consistent with this result. The limit of about 20% conversion, which we have not been able to exceed, implies, therefore, that the reaction is diffusion controlled and that only molecules which begin as fairly close neighbors can diffuse together on annealing. This conclusion receives further support from the results of annealing matrices containing partially oriented CpN_2. Warming to temperatures at which fulvalene is readily formed from Cp: (20–35 K) caused no significant reduction in IR linear dichroism, implying that the molecules of CpN_2 could not rotate in the matrix. While it may be argued that CpN_2 is a bulkier molecule than Cp:, it is hard to reconcile complete rotational immobility of the former with facile long-range translational diffusion of the latter. It is more likely that a molecule of Cp: can rotate fairly easily in its own plane and nudge its way into neighboring substitutional sites in the matrix, and that this limited motion is enough to account for the observed dimerization.

When CpN_2 is photolyzed in pure CO matrices, the ketene, CpCO (**4**), seems to be formed exclusively, presumably via the carbene. In CO-doped N_2 matrices, on the other hand, both Cp: and CpCO are generated, and the thermal reaction between Cp: and CO can be observed on annealing. This reaction proceeds more readily than dimerization of Cp:, which is to be expected if molecules of CO are more mobile than the larger molecules of Cp: and also present in large excess. We have so far been unable to demonstrate unequivocally that CpCO dissociates photolytically. This reaction differs from the photodissociation of CpN_2 in that recombination of Cp: and CO can occur in the matrix, while that of Cp: and N_2 does not. It is likely, therefore, that the reluctance of CpCO to decompose to Cp: and CO when irradiated at 254 nm reflects facile cage recombination rather than an unreactive excited state.

The dimerization of Cp: and its reaction with CO are the only thermal reactions of this species that we have observed in matrices at 10–35 K. To these must be added the reaction of Cp: with O_2, which has recently been reported[10] to yield various carbonyl compounds via the intermediate carbonyl oxide, $Cp{=}O^{+}{-}O^{-}$. The carbene is apparently unreactive at these temperatures toward CH_4 (no C—H insertion) and CpN_2 (no formation of Cp_2 or Cp=N—N=Cp).

The photolysis of Cp: is an interesting reaction, which at present serves merely as a fourth process enabling us to correlate UV and IR bands of the carbene. The product (**6**) remains for the moment unidentified, although its IR spectrum suggests a terminal alkyne structure, RC≡CH. By comparison with the photochemistry of a heterocyclic analogue,[20] 3-ethynylcyclopropene is a strong possibility, but we have insufficient data to decide between the alternatives. This and analogous reactions are currently the subject of further study.

Photolysis with Plane-Polarized Light. The experiments involving plane-polarized irradiation have provided examples of three phenomena: photoselection, photoorientation, and photoreorientation.[21] We shall discuss these by considering a beam of x-polarized light propagated in the z direction. Molecules whose photoactive transition moment vectors lie along the x, y, or z directions will be described as x-, y-, or z-oriented, respectively.

(i) **Photoselection.** x-Polarized irradiation of molecules of CpN_2 held rigidly in the matrix results in the preferential photolysis of x-oriented molecules. Consequently, as photolysis proceeds, the residual molecules of CpN_2 tend to the y- or z-oriented direction. Substantial degrees of polarization can be attained in this way (Figures 5 and 6).

(ii) **Photoorientation.** When x-polarized photolysis of CpN_2 is carried out in CO matrices, the outcome is selective depletion of x-oriented CpN_2 molecules and the preferential formation of x-oriented CpCO molecules. Presumably, the reaction occurs via the carbene, and if all the species involved (CpN_2, Cp:, and CpCO) remained rigidly fixed in the matrix, the measured absorbance for the photooriented CpCO and photoselected CpN_2 at each stage of the reaction would be related to the extinction coefficients (ϵ_{CpCO} and $\epsilon_{\mathrm{CpN_2}}$) by the equation:

$$(A_{\parallel} - A_{\perp})_{\mathrm{CpCO}}/(A_{\perp} - A_{\parallel})_{\mathrm{CpN_2}} = \epsilon_{\mathrm{CpCO}}/\epsilon_{\mathrm{CpN_2}}$$

It is obvious (Figure 5) that this relationship does not hold for the conversion of CpN_2 into CpCO. The implication, therefore, is that molecules of CpCO or, more probably, the intermediate carbene gain enough energy to rotate within the matrix. The fact that molecules of CpCO do retain some net orientation, however, suggests that rotation of the molecules and reaction of Cp: with CO occur at comparable rates.

(iii) **Photoreorientation.** When CpCO in a CO matrix is irradiated in its absorption band with x-polarized light, there is apparently no chemical reaction. Instead, the molecules undergo reorientation, tending to accumulate in orientations with a low probability of reabsorption (y and z orientations).[22] This tendency is manifest in two ways: (a) a decrease in the overall absorption intensity of the sample (Figures 7a and 7b) and (b) linear dichroism (Figures 7b and 7c). The former observation deserves comment because such a decrease in the sample absorbance is usually taken to imply a photolytic process. That this is not the case here is evident from the facts that no new UV absorption belonging to a product is observed and that the decrease in absorbance occurs rapidly at the start, but afterwards little further

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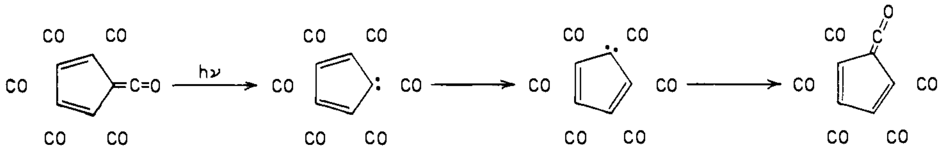
(22) An example of the principle of Le Chatelier.

Scheme II



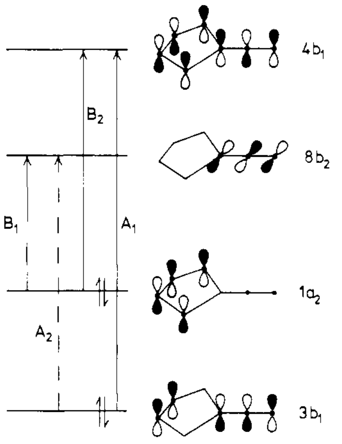


Figure 8. Schematic molecular orbitals of CpN_2 from extended Hückel calculations.

decrease is observed, even when the irradiation is continued with y-polarized light. In principle, alternate irradiation with x- and y-polarized light should, if sufficiently prolonged, result in a sample with the molecules predominantly z-oriented. Thus even with reorientation and no photolysis, the sum of x- and y-polarized absorbances should steadily decrease. Achieving this experimentally, however, will be limited by imperfections in the optical system and light-scattering within the matrix, both of which will produce a significant z component in the resultant E vector. A second limitation might arise from the mechanism of the reorientation itself. The most probable mechanism is shown in Scheme II. Photon absorption by CpCO results in dissociation to CO and Cp:, which may be reoriented in the cage either by rotation of the whole carbon skeleton or simply by hydrogen migration. Recombination with a CO molecule gives reoriented CpCO. If, as seems plausible, reorientation is thus confined to the plane of the ring, it would be impossible to produce from a random sample an oriented sample with negligible x- and y-polarized absorption.[21] A corollary of this interpretation of the observations is that, when a photoreorientation mechanism exists for molecules in a matrix, irradiation with collimated but unpolarized light (propagated along the z direction) should produce a sample with predominantly z-oriented molecules. This would be observed as a decrease in the sample absorbance (x- and y-polarized) and could easily be confused with photolysis. We have so far been unable to demonstrate this phenomenon in the laboratory, but its possibility introduces the need for caution in the interpretation of solid-state photochemistry.

Linear dichroism of matrix samples may be exploited in various ways. Obtaining information about the rotation of molecules during reaction or annealing and the assignment of absorption band symmetries have both been discussed in this paper and on previous occasions.[17] IR absorption band symmetries may be correlated between similar structures, thus providing useful additional evidence for structural assignments. UV-absorption-band symmetries may also be correlated with the MO description of the molecule. Figure 8 depicts the highest two occupied and lowest two unoccupied molecular orbitals of CpN_2, as obtained from EHT calculations.[23] The ordering of the occupied MO's was found to agree qualitatively with previous ab initio computations.[24] Of the four possible transitions involving these orbitals, one is symmetry forbidden (A_2) and only one ($4b_1 \leftarrow 3b_1$) is of A_1 symmetry as determined experimentally for the photoactive absorption.[25] It is pleasingly consistent with the photodissociation of CpN_2 that this transition corresponds to promotion of an electron from an orbital that has C–N bonding character to one that has C–N antibonding character.

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(24) L. J. Aarons, J. A. Connor, I. H. Hillier, M. Schwarz, and D. R. Lloyd, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1106 (1974).

(25) A reviewer has made the following point. The reason for the lowest $\pi\pi^*$ state of CpN_2 being A_1 in spite of the fact that $3b_1 \rightarrow 4b_1$ is not the lowest energy $\pi\pi^*$ configuration in Figure 8 is undoubtedly the existence of CI mixing with $1a_2 \rightarrow 2a_2$; the lowest B_2 state will similarly be a mixture of $1a_2 \rightarrow 4b_1$ with $3b_1 \rightarrow 2a_2$ (these are the two L states in Platt's notation). On the other hand, the orbital $8b_2$ may well appear at spuriously low energies in the EHT model.