

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

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**Abstract:** Diazocyclopentadiene (1) was photolyzed in N<sub>2</sub>, 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<sub>1</sub> 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<sub>2</sub>, 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).<sup>2</sup> Analysis of the ESR spectrum reveals that one unpaired electron is in the  $\pi$  system and the other is localized in an in-plane orbital at C-1. An EHT MO calculation<sup>3</sup> 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  $\pi$  orbital should lie close together (within 0.13 eV).

Nevertheless, the solution photochemistry of CpN<sub>2</sub> 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.<sup>4-7</sup> It is likely, therefore, that photolysis of CpN<sub>2</sub> 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,<sup>8</sup> 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.<sup>9</sup> The matrix reaction of 2 with O<sub>2</sub> has also been reported recently.<sup>10</sup>

## 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.<sup>11</sup> 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.

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Table I. IR Bands of CpN<sub>2</sub> (1) and CpCO (4) in CO Matrices

CpN <sub>2</sub> (1)		CpCO (4)	
$\bar{\nu}$ (cm <sup>-1</sup> )	symmetry <sup>a</sup>	$\bar{\nu}$ (cm <sup>-1</sup> )	symmetry <sup>a</sup>
2104 (vs) <sup>b</sup>	A <sub>1</sub> <sup>c</sup>	2133 (vs)	A <sub>1</sub> <sup>c</sup>
2096 (s)	A <sub>1</sub>	2130 (s)	A <sub>1</sub>
		2082 (w)	
		2079 (w)	
1583 (w)		1444 (w)	
1421 (m)	A <sub>1</sub>	1432 (m)	A <sub>1</sub>
1413 (m)	A <sub>1</sub>	1396 (w)	
1389 (m)	A <sub>1</sub>	1385 (w)	
		1380 (w)	
		1326 (w)	
1297 (m)	A <sub>1</sub>		
1275 (w)			
1228 (w)			
1075 (w)		1080 (w)	
1064 (m)	A <sub>1</sub>		
926 (w)		927 (w)	
915 (m)	A <sub>1</sub>	901 (m)	A <sub>1</sub>
725 <sup>d</sup> (s)	B <sub>1</sub> or B <sub>2</sub>	737 (m)	B <sub>1</sub> or B <sub>2</sub>
687 (w)		699 (w)	
652 (w)		640 (w)	
626 (w)			
568 (w)	B <sub>1</sub> or B <sub>2</sub>	582 (m)	
		527 (w)	

<sup>a</sup> Determined in polarization experiments. <sup>b</sup> Qualitative intensities: w = weak, m = medium, s = strong, vs = very strong. <sup>c</sup> The A<sub>1</sub> modes of both molecules are split into two components by matrix effects. <sup>d</sup> This band is at 713 cm<sup>-1</sup> in N<sub>2</sub> matrices.

Table II. IR Bands ( $\bar{\nu}$ , cm<sup>-1</sup>) of Cyclopentadienylidene (2) in N<sub>2</sub> at 20 K

1345 (w) <sup>a</sup>	922 (w)
1335 (m)	703 (s)
1101 (w)	577 (w)
1074 (w)	

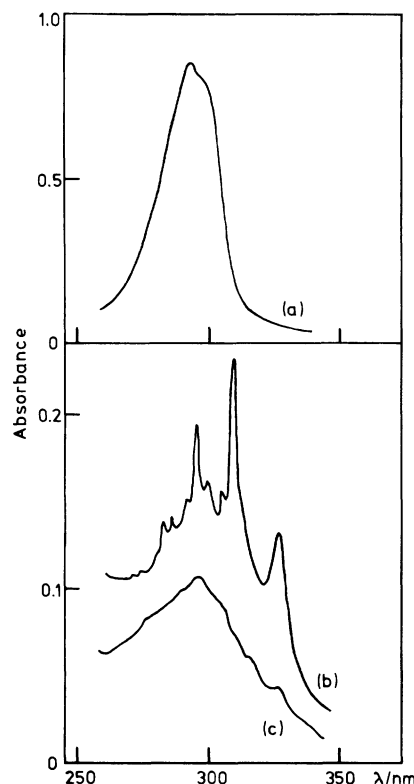
<sup>a</sup> Qualitative intensities: w = weak, m = medium, s = strong.

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.

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.<sup>12</sup> 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 ( $\lambda > 300\text{ nm}$ ),  $MR\ 10^3$ ; (c)  $CpN_2$  after complete photolysis ( $\lambda > 300\text{ nm}$ ),  $MR\ 1.5 \times 10^6$ .

cyclopentadiene<sup>13</sup> (**1**) and *o*-diazquinone<sup>14a</sup> (**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 ( $\lambda_{max}$ ) and 300 nm (shoulder) (Figure 1a). The spectrum did not alter significantly over a 1500-fold concentration range ( $MR\ 10^3$ – $1.5 \times 10^6$ ) 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  $\nu_{C-N}$  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 ( $\lambda > 300\text{ nm}$ ) 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**).<sup>8</sup> At low concentration ( $MR\ 10^4$ – $1.5 \times 10^6$ ), however, the spectrum of  $Cp_2$  was much weaker, and the principal absorption (Figure 1c) was a broad band with  $\lambda_{max}$  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  $\lambda_{max}$  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<sup>15</sup> or 1,4-pentadiyne,<sup>16</sup> 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 ( $\nu_{C-CO}$ , 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*-Diazquinone (**5**),<sup>14</sup> 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 ( $\lambda > 300\text{ nm}$ ) of **5** led to disappearance of its IR bands ( $\nu_{max}$  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 ( $\lambda\ 254 \pm 10\text{ nm}$ ) 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<sup>17</sup> 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

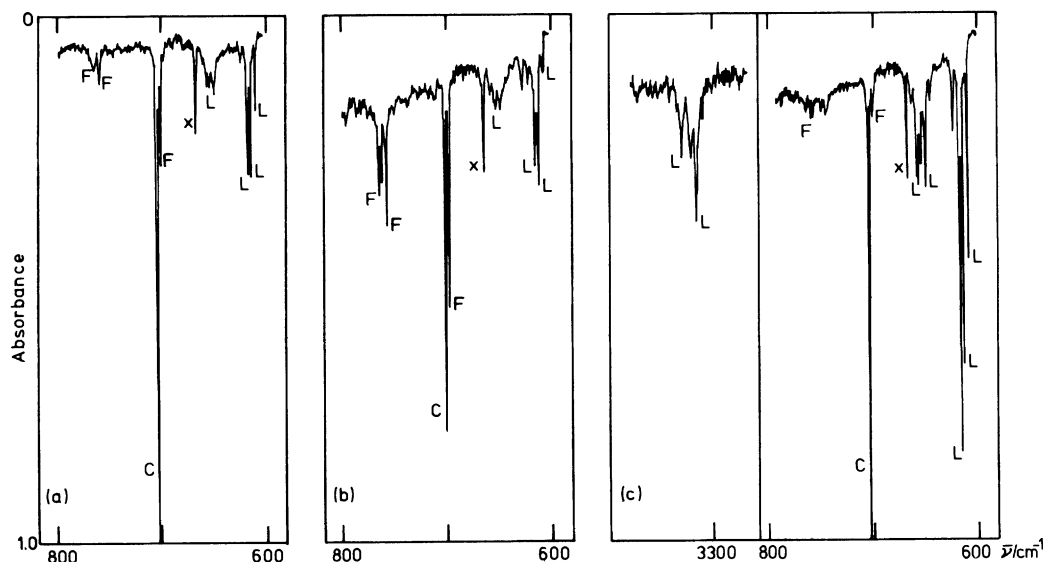
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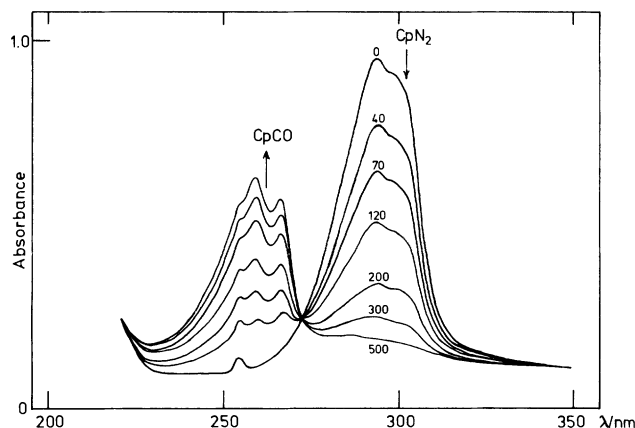
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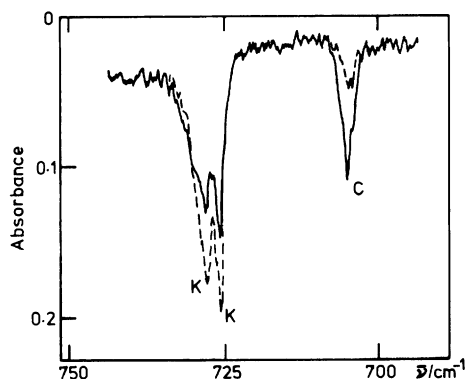
(14) (a) M. Puza and D. Doetschman, *Synthesis* 481 (1971). (b) The Ar matrix photolysis of **5** has been independently reported to yield **4** (ref 10b).



**Figure 2.** IR spectra, N<sub>2</sub> matrices at 12 K: (a) CpN<sub>2</sub> after 15-min, irradiation ( $\lambda > 310$  nm), MR  $2 \times 10^3$ ; (b) same sample after annealing at 30 K; (c) CpN<sub>2</sub> after 34-min irradiation ( $\lambda > 285$  nm), then 80 min ( $\lambda > 200$  nm), MR  $10^4$ . Band assignments: C (Cp), F (Cp<sub>2</sub>), L (6), × (CO<sub>2</sub> impurity).



**Figure 3.** UV absorption spectra showing the progress of photolysis ( $\lambda > 300$  nm) of CpN<sub>2</sub> 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  $\lambda_{\max}$  254 nm; this is present throughout and appears also in Figures 5 and 7.



**Figure 4.** IR spectra, N<sub>2</sub> matrix doped with 10% CO (12 K): (—) CpN<sub>2</sub> after 9-min photolysis ( $\lambda > 300$  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<sub>2</sub>, 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 ap-

propriate 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  $90^\circ$ .

Figure 5 shows linear dichroism in the UV spectra of residual CpN<sub>2</sub> and product CpCO in CO at 12 K, following plane-polarized irradiation ( $\lambda 315 \pm 10$  nm) in the photochemically active absorption band of CpN<sub>2</sub>. Although the absorption maximum of CpN<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> in N<sub>2</sub> at 12 K after similar polarized irradiation. The band at  $2100\text{ cm}^{-1}$  behaves in the same way as the UV absorption ( $A_\perp > A_\parallel$ ), and since this band can be confidently assigned to the  $\nu_{\text{CNN}}$  mode ( $A_1$  symmetry), it follows that the photochemically active UV absorption is also of  $A_1$  symmetry. On the other hand, the  $703\text{-cm}^{-1}$  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<sub>2</sub> 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  $703\text{ cm}^{-1}$  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<sub>2</sub>, 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<sub>2</sub> 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

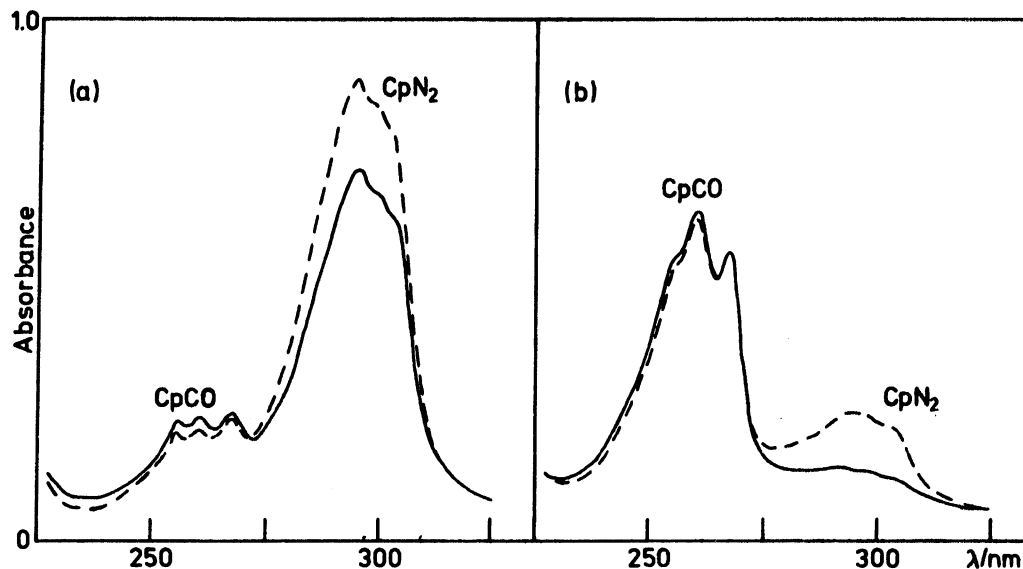


Figure 5. Linearly dichroic UV absorption spectra, CO matrix at 12 K: (a)  $\text{CpN}_2$  after 3-min photolysis with x-polarized light ( $\lambda 315 \pm 10$  nm),  $\text{MR } 10^3$ ; (b) same sample after 27-min x-polarized photolysis ( $\lambda 315 \pm 10$  nm): (—) x-polarized spectra (parallel), (---) y-polarized spectra (perpendicular).

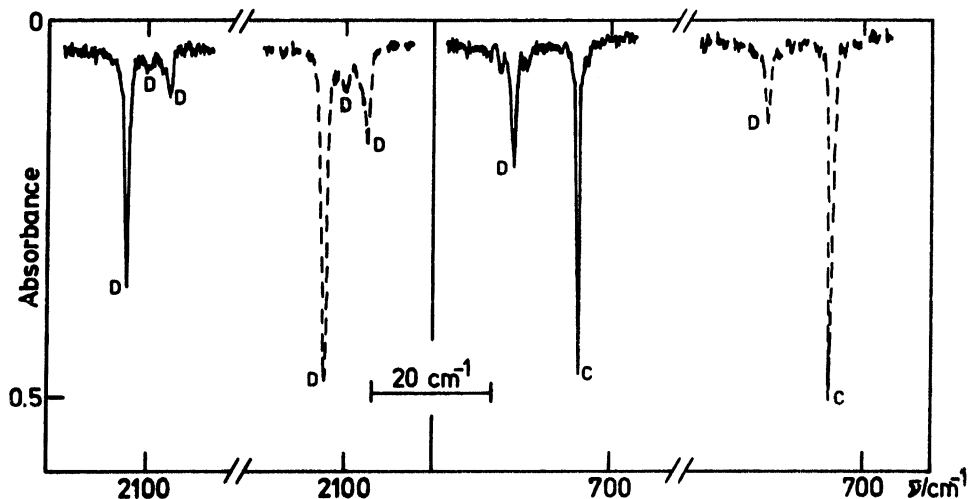


Figure 6. Linearly dichroic IR spectra,  $\text{N}_2$  matrix at 12 K.  $\text{CpN}_2$  after partial photolysis with x-polarized light ( $\lambda 315 \pm 10$  nm),  $\text{MR } 5 \times 10^{-3}$ ; (—) x-polarized spectrum (parallel), (---) y-polarized spectrum (perpendicular). Band assignments: C ( $\text{Cp}$ ); D ( $\text{CpN}_2$ ).

5 it is clear that, although  $\text{CpCO}$  could be produced with net orientation by polarized photolysis of  $\text{CpN}_2$  in CO, the degree of polarization achieved in this way was relatively small. A higher degree of polarization was achieved by irradiation of  $\text{CpCO}$  itself. Figure 7 shows the result of one such experiment. Starting with a randomly oriented sample of  $\text{CpCO}$  in CO at 12 K, irradiation with x-polarized light ( $\lambda 254 \pm 10$  nm) in the absorption band of  $\text{CpCO}$  produced a sample with  $A_y > A_x$  (Figure 7b). This process was accompanied by a slight overall loss of absorption intensity, the origin of which is discussed briefly in the next section. Subsequent irradiation of the matrix with y-polarized light reversed the direction of sample dichroism ( $A_x > A_y$ ), with little further overall loss of absorption intensity (Figure 7c). The spectra show unequivocally that, on the average, molecules of  $\text{CpCO}$  had been reoriented by this reversal of polarization, the preferred orientation having the transition moment vector perpendicular to the  $E$  vector of the irradiating light. The experiment continued for several days, during which time the direction of polarization of the sample was reversed again, with no overall loss of intensity. Thus, up to a point, the molecules of  $\text{CpCO}$  could be shepherded from one orientation to another.

From polarized IR spectra of oriented  $\text{CpCO}$  produced in this way, the band symmetries of the five strongest IR absorptions were determined relative to the  $\nu_{\text{CO}}$  band at  $2133 \text{ cm}^{-1}$  ( $A_1$ ). From these spectra it also followed that the active UV absorption of  $\text{CpCO}$  had  $A_1$  symmetry.

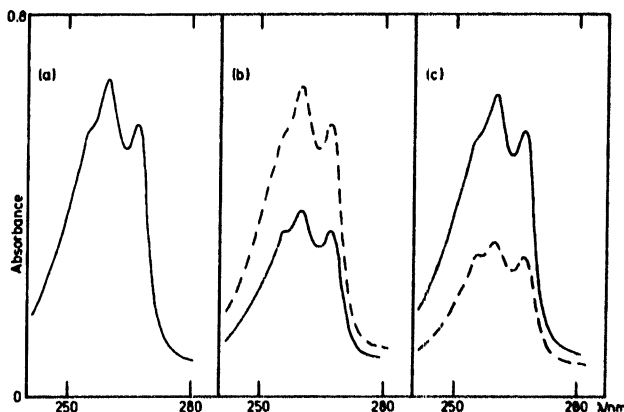
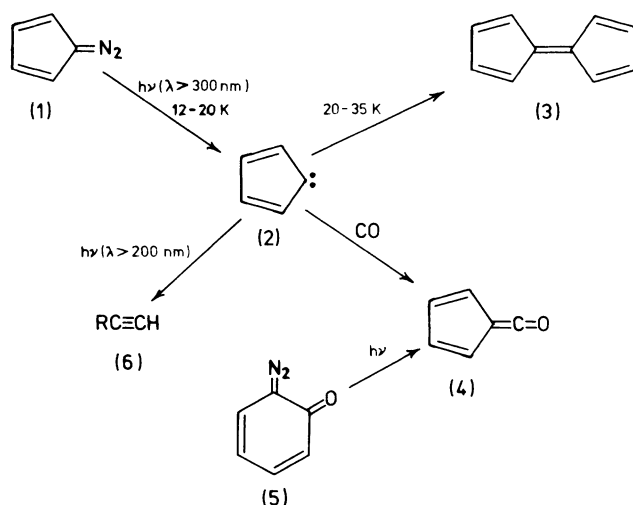


Figure 7. Linearly dichroic UV absorption spectra, CO matrix at 12 K: (a)  $\text{CpCO}$  after complete photolysis ( $\lambda 315 \pm 10$  nm) of  $\text{CpN}_2$ ,  $\text{MR } 10^3$  (the x- and y-polarized spectra were superimposable); (b) same sample after 15-h irradiation with x-polarized light ( $\lambda 257 \pm 10$  nm); (c) same sample after a further 71-h irradiation with y-polarized light ( $\lambda 257 \pm 10$  nm): (—) x-polarized spectra, (---) y-polarized spectra.

#### Discussion and Conclusions

**Reactions of the Carbene  $\text{Cp}$ : at 12–35 K.** The chemical reactions which have been observed in these matrix studies are summarized in Scheme I. The assignments of the UV absorption

Scheme I



at 296 nm and the IR bands of Table II to the carbene  $\text{Cp:}$  (2) are based on the simultaneous appearance or disappearance of these features in four processes: (i) the photolysis of  $\text{CpN}_2$ , (ii) the dimerization of  $\text{Cp:}$ , (iii) the reaction of  $\text{Cp:}$  with CO, and (iv) the photolysis of  $\text{Cp:}$  to give an unidentified alkyne (6).

The ejection of  $\text{N}_2$  from  $\text{CpN}_2$  is apparently irreversible at these temperatures, since partial photolysis of  $\text{CpN}_2$  in  $^{15}\text{N}_2$  produced no detectable amount of  $\text{Cp}^{15}\text{N}_2$ , either immediately or on subsequent annealing. In contrast, photolysis of diazomethane in  $\text{N}_2$  at 20 K results in exchange of nitrogen with the matrix host, presumably via methylene.<sup>18</sup> Hence there is a pronounced reactivity difference between these two carbenes.

The dimerization of  $\text{Cp:}$  to fulvalene occurs at 20–35 K in matrices containing little or no residual  $\text{CpN}_2$ . These conditions exclude the possibility of a reaction between  $\text{Cp:}$  and  $\text{CpN}_2$ . It has recently been pointed out that such carbene–carbene dimerizations, while energetically favorable, are exceedingly rare.<sup>19</sup> 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,  $\text{Cp:}$ , dimerizes at very low temperatures is 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  $\text{CpN}_2$ . Warming to temperatures at which fulvalene is readily formed from  $\text{Cp:}$  (20–35 K) caused no significant reduction in IR linear dichroism, implying that the molecules of  $\text{CpN}_2$  could not rotate in the matrix. While it may be argued that  $\text{CpN}_2$  is a bulkier molecule than  $\text{Cp:}$ , 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  $\text{Cp:}$  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  $\text{CpN}_2$  is photolyzed in pure CO matrices, the ketene,  $\text{CpCO}$  (4), seems to be formed exclusively, presumably via the carbene. In CO-doped  $\text{N}_2$  matrices, on the other hand, both  $\text{Cp:}$  and  $\text{CpCO}$  are generated, and the thermal reaction between  $\text{Cp:}$  and CO can be observed on annealing. This reaction proceeds more readily than dimerization of  $\text{Cp:}$ , which is to be expected if molecules of CO are more mobile than the larger molecules of  $\text{Cp:}$  and also present in large excess. We have so far been unable to demonstrate unequivocally that  $\text{CpCO}$  dissociates photolytically. This reaction differs from the photodissociation of  $\text{CpN}_2$  in that

recombination of  $\text{Cp:}$  and CO can occur in the matrix, while that of  $\text{Cp:}$  and  $\text{N}_2$  does not. It is likely, therefore, that the reluctance of  $\text{CpCO}$  to decompose to  $\text{Cp:}$  and CO when irradiated at 254 nm reflects facile cage recombination rather than an unreactive excited state.

The dimerization of  $\text{Cp:}$  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  $\text{Cp:}$  with  $\text{O}_2$ , which has recently been reported<sup>10</sup> to yield various carbonyl compounds via the intermediate carbonyl oxide,  $\text{Cp=O}^+-\text{O}^-$ . The carbene is apparently unreactive at these temperatures toward  $\text{CH}_4$  (no C–H insertion) and  $\text{CpN}_2$  (no formation of  $\text{Cp}_2$  or  $\text{Cp=N=N=Cp}$ ).

The photolysis of  $\text{Cp:}$  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,  $\text{RC}\equiv\text{CH}$ . By comparison with the photochemistry of a heterocyclic analogue,<sup>20</sup> 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.<sup>21</sup> 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  $\text{CpN}_2$  held rigidly in the matrix results in the preferential photolysis of  $x$ -oriented molecules. Consequently, as photolysis proceeds, the residual molecules of  $\text{CpN}_2$  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  $\text{CpN}_2$  is carried out in CO matrices, the outcome is selective depletion of  $x$ -oriented  $\text{CpN}_2$  molecules and the preferential formation of  $x$ -oriented  $\text{CpCO}$  molecules. Presumably, the reaction occurs via the carbene, and if all the species involved ( $\text{CpN}_2$ ,  $\text{Cp:}$ , and  $\text{CpCO}$ ) remained rigidly fixed in the matrix, the measured absorbance for the photooriented  $\text{CpCO}$  and photoselected  $\text{CpN}_2$  at each stage of the reaction would be related to the extinction coefficients ( $\epsilon_{\text{CpCO}}$  and  $\epsilon_{\text{CpN}_2}$ ) by the equation:

$$(A_{\parallel} - A_{\perp})_{\text{CpCO}} / (A_{\perp} - A_{\parallel})_{\text{CpN}_2} = \epsilon_{\text{CpCO}} / \epsilon_{\text{CpN}_2}$$

It is obvious (Figure 5) that this relationship does not hold for the conversion of  $\text{CpN}_2$  into  $\text{CpCO}$ . The implication, therefore, is that molecules of  $\text{CpCO}$  or, more probably, the intermediate carbene gain enough energy to rotate within the matrix. The fact that molecules of  $\text{CpCO}$  do retain some net orientation, however, suggests that rotation of the molecules and reaction of  $\text{Cp:}$  with CO occur at comparable rates.

**(iii) Photoreorientation.** When  $\text{CpCO}$  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).<sup>22</sup> 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

(18) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **41**, 3504 (1964).

(19) L. M. Cheung, K. R. Sundberg, and K. Ruedenberg, *J. Am. Chem. Soc.*, **100**, 8024 (1978); *Int. J. Quantum Chem.*, **16**, 1103 (1979).

(20) W. L. Magee and H. Schechter, *J. Am. Chem. Soc.*, **99**, 633 (1977).

(21) For a more general discussion of photoselection, see A. C. Albrecht in "Progress in Reaction Kinetics", Vol. 5, G. Porter, Ed., Pergamon, Oxford, 1970.

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

Scheme II

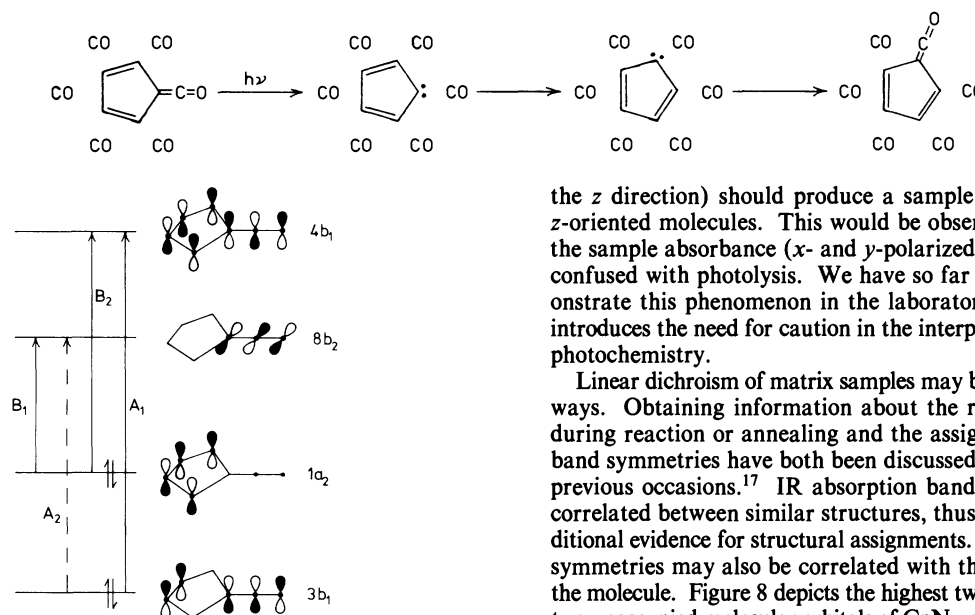


Figure 8. Schematic molecular orbitals of  $\text{CpN}_2$  from extended Hückel calculations.

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  $\text{CpCO}$  results in dissociation to  $\text{CO}$  and  $\text{Cp:}$ , which may be reoriented in the cage either by rotation of the whole carbon skeleton or simply by hydrogen migration. Recombination with a  $\text{CO}$  molecule gives reoriented  $\text{CpCO}$ . 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.<sup>21</sup> 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.<sup>17</sup> 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  $\text{CpN}_2$ , as obtained from EHT calculations.<sup>23</sup> The ordering of the occupied MO's was found to agree qualitatively with previous *ab initio* computations.<sup>24</sup> 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.<sup>25</sup> It is pleasingly consistent with the photodissociation of  $\text{CpN}_2$  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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(23) We thank Dr. J. K. Burdett for carrying out the calculations.

(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  $\text{CpN}_2$  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.