BENT CYCLOPENTA-2,4-DIENYLIDENEKETENE: SPECTROSCOPIC AND *ab initio* STUDY OF REACTIVE INTERMEDIATE

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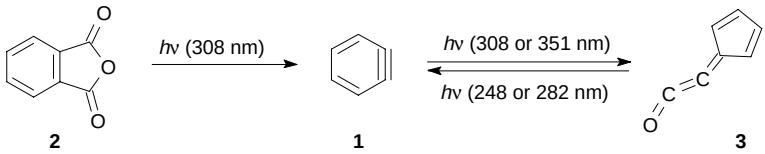
Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

Results of an experimental and theoretical study of cyclopenta-2,4-dienylideneketene (**3**), a highly unstable reactive intermediate, are reported. The ketene was prepared, under matrix isolation conditions at 4.2 or 10 K, by laser photocarbonylation of 1,2-didehydrobenzene (**1**) photogenerated earlier from phthalic anhydride (**2**). FTIR polarization measurements performed on partially photooriented samples of **3** immobilized in solid neon or argon provide infrared transition moment directions for most of the observed vibrations. Experimental results confirm that the ketene is bent, as predicted by *ab initio* calculations. Utilizing two isotopically modified **3**, **3b** and **3c**, on the basis of the infrared absorption spectrum alone, we have analyzed and assigned its vibrations in a way, which leaves no doubt about the bent ketene structure. This work was motivated by a long standing confusion surrounding the assignments of the vibrations in 1,2-didehydrobenzene (**1**), especially of its "triple" bond stretch.
Key words: Matrix isolation; Photolysis of phthalic anhydride; IR spectrum of cyclopenta-2,4-dienylideneketene; Ketenes; Benzyne; *Ab initio* Calculations.

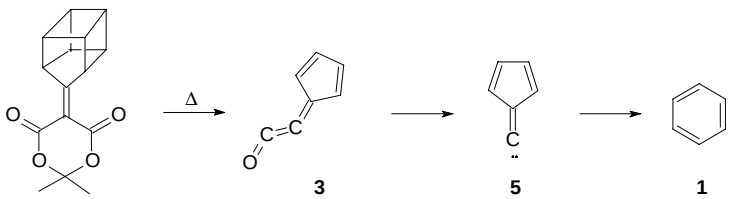
In a recent IR study[1] of 1,2-didehydrobenzene (benzyne) (**1**) we reported that irradiation of phthalic anhydride (**2**) in various matrices led to the formation of a mixture of **1** and a second compound for which we proposed the structure cyclopenta-2,4-dienylideneketene (**3**) (Scheme 1). This proposal was based, in part, on the computed (SCF/6-31G*) infrared spectrum of **3**. We also demonstrated that this mixture could be converted to essentially pure **1** by irradiation with light of shorter wavelength than that used to produce the mixture of **1** and **3** from **2**.

In this paper, we report a detailed infrared study of **3** and comparison of its infrared absorptions with *ab initio* predictions.



SCHEME 1

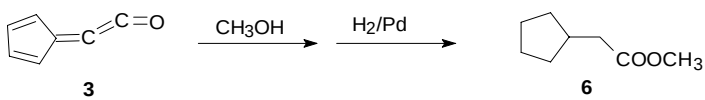
While **3** has never been definitively characterized, it has been proposed as a reactive intermediate in a number of earlier studies. Brown[2] first proposed **3** as an intermediate in the pyrolysis of **4** (Scheme 2), which subsequently lost carbon monoxide to yield cyclopenta-2,4-dienylidenecarbene (**5**), which in turn rearranged to **1**. The presence of **1** as an intermediate in the pyrolysis was deduced from the composition of the product mixture. Subsequently, Brown[3] also suggested the possible intermediacy of **3** in the formation of **1** in the pyrolysis of **2**.



SCHEME 2

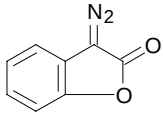
In 1986 Brown[4] reported that the pyrolysis products of **4**, trapped in an Ar matrix, exhibited infrared absorptions characteristic of ketenes (2 226, 2 203 and 2 090 cm^{-1}). From the absence of these bands in the spectrum of the pyrolysis products of **2**, he suggested that **2** underwent a concerted fragmentation to give **1** directly, without the intermediacy of **3**. However, the results of a similar study, reported in 1988 by Wentrup[5], indicated that **3** might be an intermediate between **2** and **1**.

Further spectroscopic evidence for the intermediacy of ketene **3** in the pyrolysis of **4** was presented by Brown[6]. He attributed a number of IR bands to ketene **3**. He also provided chemical evidence for the existence of **3** by treating the pyrolysate with methanol followed by catalytic hydrogenation, which yielded the ester **6** (Scheme 3).



SCHEME 3

Schweig[7] in 1989 proposed **3** as possible side product in the photochemical conversion of **7** and **8** to 1,2-didehydrobenzene. In a subsequent detailed photochemical study[8], he proposed that **8** first underwent conversion to cyclopropabenzen-1-one, which in turn could be photolyzed to give mixtures of **1** and **3**. It was further shown that



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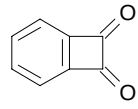

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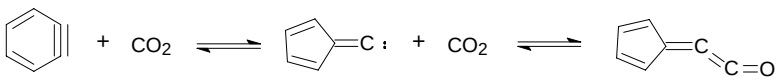
1 and **3** could be photochemically interconverted in an argon matrix through the presumed intermediacy of the carbene **5** (Scheme 4). This result is similar to that mentioned above by us[1].



1 **5** **3**

SCHEME 4

In spite of the numerous studies which have dealt with **3**, it has yet to be fully characterized spectroscopically. Our finding that the mixture of **1** and **3** produced in the photolysis of **2** could be converted photochemically to essentially pure **3** provided us with the means to carry out a detailed IR spectral study of **3**. In order to aid the interpretation of the IR spectrum of **3**, we carried out *ab initio* studies of the structure and vibrational spectrum of **3** and several isotopically modified **3**. In the course of this study Scheiner and Schaefer[9] published results of their *ab initio* treatment of **3**. Their study was based only on the C_{2v} structure of **3**, even though their vibrational analyses, at both the SCF and MP2 levels, gave one imaginary frequency. Hence their reported frequencies and intensities were for a transition structure rather than the structure of the true minimum for **3**. As discussed below, we were able to locate a minimum with C_s symmetry, and carried out a vibrational analysis for this minimum structure of **3** and two isotopically modified **3**.

RESULTS AND DISCUSSION

Calculations of Geometry, IR Frequencies, Intensities and Transition Moment Directions

Using the SCF/6-31G* basis set and Gaussian 94 package[10], we initially carried out the geometry optimization of **3** with a C_{2v} symmetry constraint. With this constraint, a minimum was found (E = –342.150736 a.u.). The presence of one imaginary frequency

(14*i* cm^{-1}) in the calculated spectrum of **3** indicated that it was a transition structure rather than a real minimum. Examination of that normal mode suggested that at the real minimum the molecule would be planar with the ketene part bent. Geometry optimization carried out with only a C_s symmetry constraint, indeed led to a new minimum (E = –342.150761 a.u.). It is shown in Fig. 1. The vibrational analysis of it now gave all real frequencies (Table I). While this result at first sight might seem surprising, we note that unsubstituted propadienone (ketene) (**9a**) has been predicted to be bent[11–13], and this has been confirmed experimentally[14]. Interestingly, at the SCF level, **9a** is predicted to be "linear" (C_{2v}) but at the MP2 level bent. Difluoropropadienone (difluoroketene) (**9b**) is predicted to be bent even at the SCF level[15,16].

These results prompted us to carry out an MP2/6-31G* optimization of **3**, and the resulting structure is given in Fig. 1. It predicts **3** to be bent to a greater degree than does the SCF optimized structure. The C=C=C angle is computed to be 136.8° and the C=C=O angle 167.0°. These angles are quite similar to those found experimentally for **9a**: 144.5 and 169.4°, respectively[14].

Finally, vibrational analysis at SCF/6-31G* level was also performed for two isotopically modified **3**, (1-[^{13}C]cyclopenta-2,4-dienylidene)(2-[^{13}C]ketene) (**3b**) and ([$^{2}H_4$]cyclopenta-2,4-dienylidene)ketene (**3c**). The unlabelled **3** will be referred to as **3a**. Calculated frequencies and intensities for **3a**, **3b** and **3c** are given in Table I. Cross-correlation between calculated frequencies for the normal modes in **3a** and **3b**, as shown in Table I, is unique even without analysis of component motions of the normal modes. This originates in the fact that the two ^{13}C labels introduced to **3b** constitute only a small and very localized perturbation in the vibrating system. They affect, as desired, mainly the ketene and carbonyl stretching frequencies in the molecule. For the remaining modes, calculated shifts are small and the correlation is trivial. Both inten-

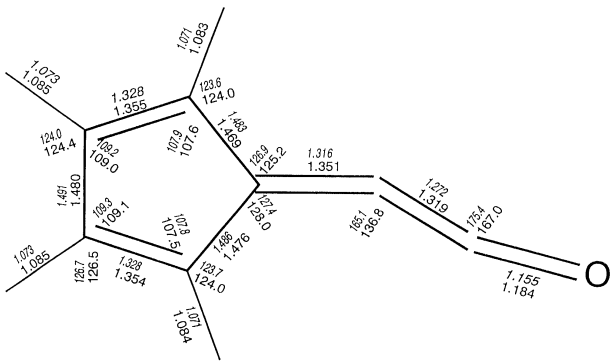


FIG. 1
The optimized structure of **3** at the SCF/6-31G* level (given in italics) and at the MP2/6-31G* level

TABLE I
IR active vibrations of cyclopenta-2,4-dienylideneketene[a] **3**

ν	**3a**						**3b**								**3c**								Assignment[c]
	Experimental			Calculated[b]			Experimental				Calculated[b]				Experimental				Calculated[b]				
	$\tilde{\nu}$	*I*	ϕ	$\tilde{\nu}$	*I*	ϕ	$\tilde{\nu}$	Δ	*I*	ϕ	$\tilde{\nu}$	Δ	*I*	ϕ	$\tilde{\nu}$	Δ	*I*	ϕ	$\tilde{\nu}$	Δ	*I*	ϕ	
1	3144	5.6	10	3447	6.9	17	3144	0	5.1	10	3447	0	7.1	17	2358	786	0.3	–	2576	871	0.9	11	C–H(D) str
2	3129	5.9	80	3443	6.1	–66	3129	0	5.0	80	3443	0	6.1	–75	2352	777	0.3	–	2569	874	4.3	–71	C–H(D) str
3	3112	2.5	(+)	3417	8.1	4	3112	0	2.5	(+)	3417	0	8.1	4	2330	782	2.0	(+)	2523	894	5.7	5	C–H(D) str
4	3104	2.0	90	3406	5.7	–89	3104	0	2.6	90	3406	0	5.7	–89	2323	781	0.5	–	2516	890	4.0	–62	C–H(D) str
5	2085	1710	6	2439	2906	8	2068	17	1620	9	2415	24	2879	8	2091	–6	1695	6	2438	1	2904	8	=C=C= str
6	1674	8.5	16	1966	23.5	27	1612	62	5.0	40	1909	57	5.3	50	1666	8	7.4	12	1965	1	23.9	27	=C=O str
7	1513	0.7	40	1802	0.1	30	1505	8	0.7	20	1802	0	0.1	27	1441	72	1.8	60	1728	74	0.5	76	$C_{2,3}$–$C_{4,5}$ str
8	1502	8.1	10	1737	15.6	–1	1499	3	13.1	10	1736	1	17.5	–1	1475	27	14.9	0	1692	45	22.8	–1	$C_{2,3}$–$C_{4,5}$ str
9	1354	43.4	10	1516	34.0	1	1353	1	41.7	15	1514	2	31.4	1	1213	141	31.7	20	1354	162	33.9	4	H wag + ring str
10	1290	8.0	30	1442	1.2	52	1287	3	7.7	40	1440	2	0.8	50	1172	118	10.1	50	1308	134	11.9	69	H(D) wag + C_1–$C_{2,3}$ str
11	1141	5.9	(+)	1281	3.8	13	1129	12	10.4	(+)	1262	19	2.6	11	1096	45	6.4	(+)	1224	57	0.1	–8	H_{11}–H_{12} wag + ketene str
12	1147	27.4	85	1273	10.8	66	1123	24	17.5	85	1248	25	8.2	64	948	199	0.3	–	1076	97	5.3	66	C_1–$C_{2,3}$ str + C_1–$C_{2,3}$–$C_{4,5}$ bend
13	1079	18.6	85	1207	9.4	78	1076	3	20.0	80	1205	2	11.4	77	892	187	9.2	70	900	307	3.1	–86	H(D) wag + $C_{2,3}$–$C_{4,5}$ str
14	1050	3.0	(–)	1168	0.2	–28	1038	12	2.0	(–)	1156	12	0.2	–27	842	208	0.6	–	863	305	0.4	25	H (D) wag + C_1–$C_{2,3}$ str
15	969	3.4	y	1083	0.1	y	968	1	3.5	y	1083	0	0.1	y	809	160	1.0	–	900	183	0.1	y	H(D) wag
16	951	3.7	y	1074	0.4	y	949	2	3.7	y	1074	0	0.4	y	814	137	4.2	y	874	200	14.4	y	H(D) wag
17	880	4.5	(+)	1033	12.2	2	879	1	5.2	(+)	1032	1	12.2	2	782	98	5.1	–	951	82	18.4	1	C_4–C_5 str
18	858	2.1	(+)	946	13.7	2	858	0	2.2	(+)	945	1	14.1	2	–				798	148	1.4	4	C_1–$C_{2,3}$ str + C_2–C_1–C_3 bend
19	782	60.0	y	895	111	y	774	8	48.4	y	885	10	112	y	683	99	10.8	y	787	98	46.8	y	H(D) wag + ring torsion
20	775	0.4	y	841	0.3	y	772	3	0.2	y	841	0	0.4	y	574	201	0.1	–	656	185	0.6	y	H(D) wag
21	770	2.0	–	833	1.8	–74	766	4	2.1	–	829	4	1.6	–73	759	11	4.7	–	790	43	0.9	–72	C_1–$C_{2,3}$–$C_{4,5}$ bend + C_1–$C_{2,3}$ str
22	648	41.0	y	736	11.1	y	648	0	43.5	y	727	9	15.9	y	647	1	39.2	y	720	16	15.5	y	ring torsion + $H(D)_{11,12}$ wag
23	612	22.0	y	681	40.1	y	606	6	18.7	y	671	10	33.1	y	494	118	26.4	y	552	129	35.9	y	=C=C=O bend + ring torsion
24	592	8.8	70	559	38.1	82	582	10	9.1	70	557	2	36.9	84	578	14	10.9	65	556	3	40.3	84	=C=C=O bend
25	497	3.0	y	543	0.6	y	494	3	1.9	y	543	0	0.6	y	–				463	80	0.2	y	ring torsion
26	521	0.3	–	527	2.5	–65	520	1	0.5	–	525	2	1.8	–62	–				514	13	0.8	–43	C_2–C_1–C_3 bend + ketene str
27	434	3.7	–	436	17.2	59	426	8	1.9	–	427	9	17.0	59	411	23	1.0	–	414	22	16.0	58	ketene wag + =C=C=O bend
28	257	0.5	–	281	0.7	y	254	5	0.4	–	276	5	0.7	y	244	16	0.1	–	270	11	0.5	y	ring torsion + ketene wag
29	–			107	0.1	y	–				105	2	0.1	y	–				102	5	0.1	y	ring torsion + ketene wag
30	–			30	2.7	53	–				30	0	2.6	53	–				29	1	2.4	51	ketene bend

[a] Neon matrix; $\tilde{\nu}$ in cm^{-1}; *I* absolute intensity in km/mol; all observed and calculated isotopic shifts (Δ in cm^{-1}), with exception of ν_5 in **3c** are to the red; ϕ transition moment angle in degrees. [b] SCF/6-31G*, no scaling. [c] Approximate mode description (see the text); str stretch; atom numbering is shown in Fig. 5.

sities and transition moment directions of all normal modes change only slightly. Similar correlation between the vibrational frequencies of **3a** and **3c** requires more careful inspection of the normal modes. For the six vibrations with the highest frequencies and seven with the lowest ones, the cross-correlation is again trivial and unique. For the reminder of the calculated vibrations, by analyzing the motions involved in each normal mode, we were able to assign and properly correlate them for **3a** and **3c**. Actual correlation is made on the basis of visual comparison of the motions constituting each normal mode[17]. The task is made simpler by treating modes of different kinds separately, *e.g.*, torsional in-plane modes in **3a** will correlate only with the same kind of modes in **3c**, *etc*. The final result is unique. We will consider an example to show how this is done. All 30 calculated modes split into two classes: 21 vibrations belong to a′ class and occur in the molecular plane, and 9 are out-of-plane ones and belong to a″ class. The a′ (in-plane) vibrations can be further divided into two subclasses: (i) a group in which torsional motions are dominant (1 442, 1 273, 434 cm^{-1}); (ii) a group in which various "symmetric" stretches and bends dominate the normal modes (the remaining in-plane polarized vibrations). The 1 442 cm^{-1} mode can be more precisely described as a stretch of the C_1–C_2 bond antisymmetric with respect to the C_1–C_3 bond, and coupled with bending of angles between carbons 2, 1, and 6 and 3, 1, and 6 (atom numbering is shown in Fig. 5). These motions are coupled with "in-phase" bending of all hydrogens. At the same time, atoms 6, 7, and 8 almost do not move. This normal mode corresponds to the 1 308 cm^{-1} vibration in **3c**.

We have inspected and analyzed the motions of all atoms for the remaining normal modes in **3a** and **3c**. The cross-correlated results are presented in Table I and were used as a guidance in assignments and correlation of the actually observed absorptions. Complete theoretical spectra are also presented in Fig. 2, for the parent and deuterated compounds mainly to facilitate comparison with the experimental results. Here, however, to make visual comparison easier for the reader, we have scaled all harmonic frequencies by the arbitrary factor of 0.94.

Experimental IR spectra

We have previously reported[1] infrared frequencies for only the cumulative double bond stretch (ketene stretch) in **3a**, **3b** and **3c**. Complete results of that study are now presented in Table I and Fig. 3, and are compared with our calculations. For the 30 fundamental vibrations predicted for **3**, we were able to identify 28. The two lowest-frequency vibrations lie outside the range of our instrument. Several weaker bands were also found in spectra of each of the isotopically modified **3**. They are most likely combination bands or overtones. The observed bands, listed in Table I, can be divided into two classes: 21 polarized in the molecular plane and 7 polarized out-of-plane. In the experimental spectra, we compare isotopic shifts of **3b** and **3c** with respect to unlabelled **3a**. The small frequency shifts induced by ^{13}C labels in **3b** make the correlation

with **3a** straightforward. By far the most intense band in the observed spectra is the =C=C=O (cumulative double bonds) stretch. In a neon matrix, it shifts from 2 085 cm^{-1} in **3a** to 2 068 cm^{-1} in **3b** and to 2 091 cm^{-1} in **3c**. Its position (the maximum of the most intense component of the observed multiplet) depends strongly on the host material. For **3a** we have recorded the following frequencies: Ne 2 085 cm^{-1}, Ar 2 080 cm^{-1}, Xe 2 073 cm^{-1} and N_2 2 082 cm^{-1}. The shape of this absorption band in several different matrices is presented in Fig. 4. In all matrices used in this study, this absorption exhibits a very complicated pattern, typical of the cases where an extremely strong vibration undergoes Fermi resonance with very weak overtones or combination bands of the lower-frequency fundamental vibrations. The resulting pattern is additionally complicated by matrix site effects and coupling with matrix phonons. It also depends, although to a lesser degree, on the particulars of the sample preparation like condensation speed, state of annealing, degree of aggregation, *etc*. Such splittings make comparison between results obtained in different matrices more difficult and unique determination of exact numerical values of the isotopic shifts is somewhat more complicated.

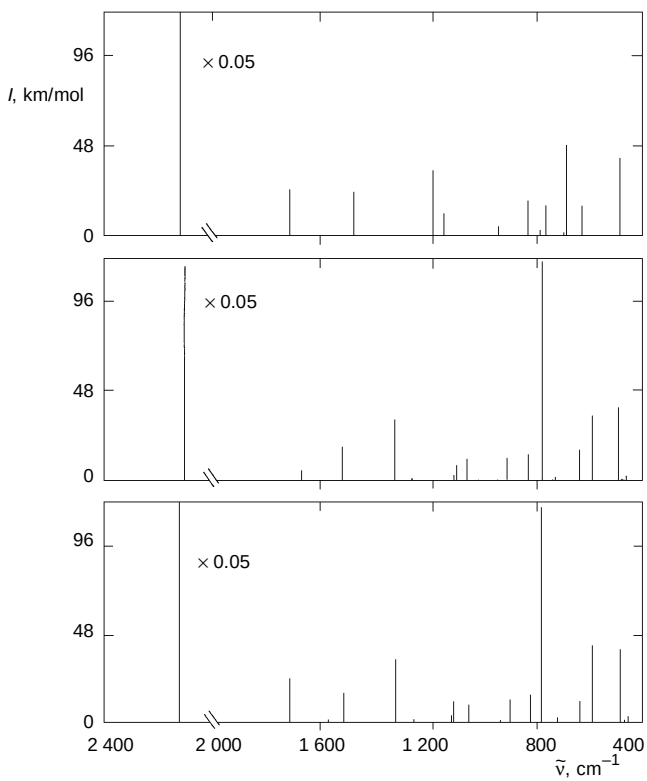


FIG. 2
Computed (SCF/6-31G*) spectra of **3a** (bottom), **3b** (center) and **3c** (top). All calculated frequencies were scaled by an arbitrary factor of 0.94 in these plots

We have also recorded the IR spectrum of mono ^{13}C-labelled **3** in α position (**3d**). In an argon matrix the most intense component of the ketene stretch appears at 2 038 cm^{-1}. Two other, slightly less intense parts of this absorption are at 2 043 and 2 033 cm^{-1}. An observed frequency shift between **3a** and **3d** of 47 cm^{-1} is in an excellent agreement with the shift of 55 cm^{-1} anticipated by theory (SCF/6-31G*). Similarly, like for all three **3a**–**3c**, an observed intensity for this extremely strong ketene band is lower (1 980 km/mol) than the one predicted by the theory (2 744 km/mol).

In agreement with theory, we do not observe any influence of ^{13}C labelling in **3b**, neither on C–H stretches nor on most of the other bands. A small frequency shift caused by these labels makes only minute changes in the nature of most of the normal modes, and thus only small differences in frequencies, intensities and transition moment directions are observed. This makes the assignments and correlation with unlabelled compound **3a** trivial. The selective and large influence of these labels on only a few vibrations coupled with the ketene stretch facilitates their assignments. The band observed in **3a** at 1 674 cm^{-1} shifts to 1 612 cm^{-1} in **3b**, and to 1 666 cm^{-1} in **3c**. We assign it as a predominantly =C=O stretch.

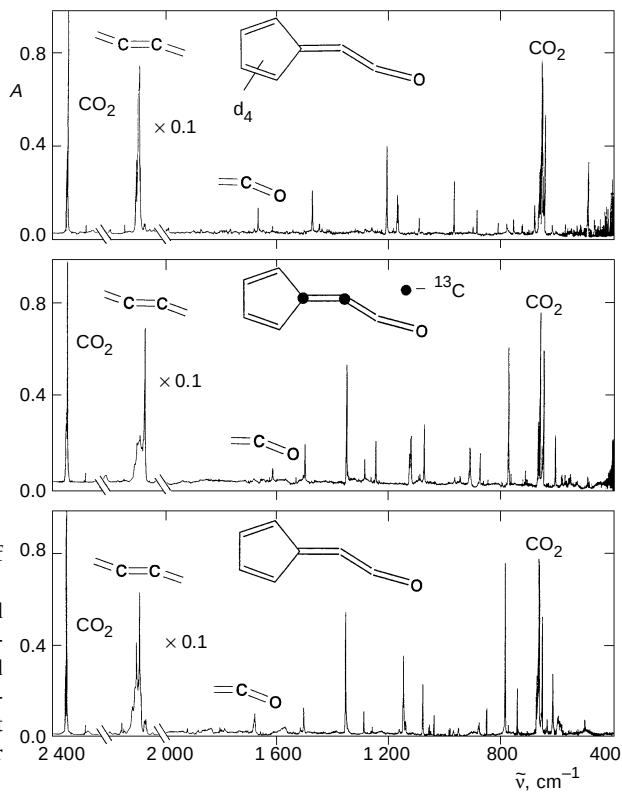


FIG. 3
Infrared absorption spectrum of cyclopenta-2,4-dienylideneketene (bottom), di-^{13}C-labelled compound (center) and perdeuterated compound (top) isolated in Ne matrix at 6 K. Peaks belonging to the residual amount of **1** were removed by computer subtraction

For most of the observed bands of **3**, we have determined absolute infrared intensities by means of calibration with an internal CO_2 standard[1]. Intensities determined from integration of each band in **3a**, **3b** and **3c** and comparison with the known absolute intensity for carbon dioxide are listed in Table I. Carbon dioxide is generated from **2** in an equimolar quantity with **3**, under conditions of full conversion of **2** and **1** to **3**. When **2** is completely converted into the mixture of ketene and benzyne, their relative concentrations can be determined from the ratio intensities of CO and CO_2. As expected, the agreement with the theoretically predicted values is quite good for stronger bands, but it diminishes somewhat for weaker ones. It also seems to be better for modes that are coupled to a lesser degree with others, *e.g.*, for both the very strong ketene stretch and weak carbonyl stretch, absolute intensities are reproduced by theory surprisingly well, even at the modest SCF level employed in this study. The intensity of the ketene stretch, determined experimentally with maximum 20% error bars is overestimated by theory. However, not surprisingly, this vibration, being over an order of magnitude stronger than any other band in the spectrum of **3**, and also three orders of magnitude stronger than the "triple" bond stretch in **1**, was repeatedly confused with the triple bond absorption and misassigned in earlier work.

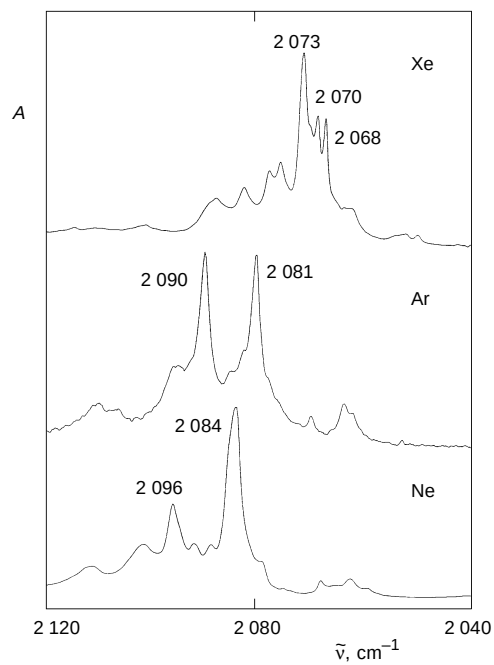


FIG. 4
Ketene stretch region in **3a** in Xe (top), Ar (center) and Ne (bottom) matrices, respectively. Spectra of **3a** in Xe and Ar were recorded with samples kept at 12 K and in Ne at 6 K

Infrared Transition Moment Directions

For the majority of the observed bands, in addition to absolute intensities, we have determined infrared transition moment directions from the polarization measurements on partially photooriented samples. In some cases, we were only able to obtain a reproducible sign ($E_Z - E_Y$, given in parentheses in Table I), but not the value of the dichroism, and for a small number of the weakest bands even the sign of the dichroism could not be determined reliably. Despite the simplicity of both the theoretical and experimental procedures involved, there are still just a few literature examples of transition moment determination for the low-symmetry reactive intermediates[18]. It should be emphasized that such measurements do not give access to molecular geometry (angles or bond distances), but only provide information about transition moment directions. Knowledge of those, however, can be used in molecular symmetry determination and qualitative estimates of some of the geometrical parameters.

Infrared transition moment directions were determined in a way described in the literature[19]. We have used the labelling of molecular axes, as marked in Fig. 5: *y* out-of-plane, *z* along the =C=C= stretch and *x* in-plane, perpendicular to *z*. In the laboratory coordinate system, light propagates along direction *X* and is linearly polarized along the *Z* axis. Using in the first step unpolarized ultraviolet light (308 and 351 nm, excimer laser or 356 nm Ar-ion laser), we have converted most of the initially generated 1,2-

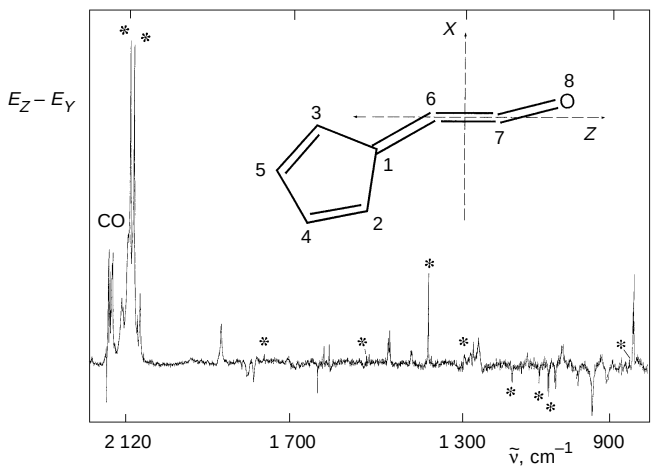


FIG. 5

Segment of a difference ($E_Z - E_Y$) between polarized infrared absorptions measured after polarized irradiation at 248 nm of Ar matrix containing **3a** and trace of **1**. Bands originating in **3a** are marked with asterisks. Remaining unmarked bands belong to **1a** and **2a**. The insert depicts orientation of molecular axes and atom numbering

didehydrobenzene (**1**) to ketene **3**. Only then was the sample exposed to polarized light at 248 nm. Partial conversion of the ketene back to **1** produced an uniaxially (about the *Z* axis) oriented sample. Simultaneous polarization measurements in the UV and IR indicate that the UV transition moment is polarized approximately perpendicularly to the =C=C= stretch (negative dichroism in UV and positive dichroism in IR for =C=C= stretch). All vibrations for which the IR dichroism could be determined can be divided into two distinct classes on the basis of their dichroic ratio values: out-of-plane vibrations (all having the same dichroism) and in-plane vibrations. We have identified seven out-of-plane infrared transitions in **3a**. All of them had (within experimental error) the same dichroic ratio $d_u = E_Z/E_Y$, which was equal to 0.74. This is equivalent to $K_y = 0.27$, where $K_u = d_u/(d_u + 2)$, ($u = x, y, z$) is an orientation factor. From the definition of the uniaxial orientation, $K_y = K_z = (1 - K_x)/2$, where K_u are principal orientation factors. For all remaining observed infrared transitions *i*, polarized in the molecular plane, we have:

$$\tan^2\phi = (K_x - K_i)/(K_i - K_z).$$

Using this formula we have obtained for the three isotopomers **3a**, **3b** and **3c** in-plane polarized infrared transitions, which are complied in Table I. The angles listed in this table were obtained by averaging results from many independent measurements and are rounded to the nearest multiple of 5. The error bars are on average about 15° for angles close to 0 and 90°, and 10° for those close to 45°. This procedure does not allow for the determination of sign of the transition moments.

Just from the inspection of the experimentally determined angles (Table I), we conclude that **3** must have a bent structure. The bend of the ketene is large enough to activate the otherwise inactive infrared modes (a_2 in C_{2v} structure) and to incline in-plane transition moments away from the C_{2v} symmetry axis. In view of the results of "calibration" studies[20,21] on the quality of theoretical transition moment direction determination, the agreement between experimentally determined and predicted transition moment directions is surprisingly good, for the level of approximation applied here.

Perhaps, with the rapid advances in computing power, the quality of theoretical predictions for transition moment directions also for larger molecules will soon be sufficiently high enough to utilize them for precise vibrational assignments.

We hope that the experimental results presented above on the infrared spectroscopy of ketene, together with a similar earlier report on 1,2-didehydrobenzene will clear the confusion surrounding vibrational assignments for these compounds.

EXPERIMENTAL

Phthalic anhydride (**2**) was sublimed at 26–32 °C into a stream of noble gas (1–3 mmol/min) and condensed on a cold CsI target. The matrix isolation ratio was determined to be 1 : 700. The temperature of the spectroscopic window was maintained at 28 K for Ar, 24 K for N_2, 32 K for CO and 4.2 K for Ne matrices. During the spectroscopic measurements and laser irradiations, the matrices were kept at around 12 K, except for Ne, for which the bottom temperature of 6 K was necessary at all times. Low-temperature samples were prepared using closed-cycle two-stage refrigerators (Displex, APD Cryogenics). In photochemical transformations, we have used excimer lasers (Lambda Physik or Lumonix) generating monochromatic light at 248 nm (KrF), 308 nm (XeCl) and 351 nm (XeF). In some experiments we have used light at 356 nm from an Ar-ion laser (Coherent I-200). Polarized FTIR spectra were recorded using a Nicolet FTIR (Magna 550) and a Cambridge Physical Sciences polarizer (IPG-225). The resolution was 1 cm^{-1}. Polarized UV-VIS absorption spectra were measured on a Shimadzu 3100 spectrophotometer using Glan–Thompson polarizers.

Anhydrides **2b**–**2d** were obtained, using the standard method, by dehydration of the corresponding labelled phthalic acids with acetic anhydride. [1-^{13}C]-, [1,2-$^{13}C_2$]- and [3,4,5,6-$^{2}H_4$]phthalic acids were purchased from MSD, in 99% isotopic purity.

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