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Formation of Nitrile Ylide by Addition of Carbene with Acetonitrile in a Low-Temperature Argon Matrix

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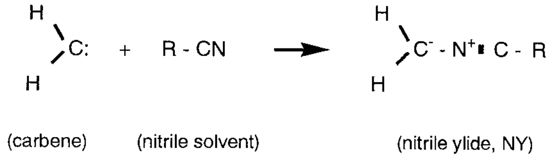
After the photoirradiation of (biphenyl-4-yl)chlorodiazirine (BCD) in ca. 10 K argon (Ar) matrices, the IR spectrum of (biphenyl-4-yl)chlorocarbene (BCC) was measured because the measured bands were in fair agreement with the bands obtained by vibration analysis. The photolyses of BCD−acetonitrile (MeCN)−Ar tricomponent matrices were also carried out to study the reaction of BCC with MeCN. For [MeCN]/[BCD] > 10, a spectrum that differed from BCC was obtained after the irradiation. The new bands are stable during the irradiation, during increasing temperature (to 45 K), and during storage. An 2-azonia-1-allenide type nitrile ylide (NY) structure was obtained in an optimization. Because the measured bands are in good agreement with those calculated using the vibration analysis for this NY structure, BCC adducts with MeCN immediately after the degradation of BCD.

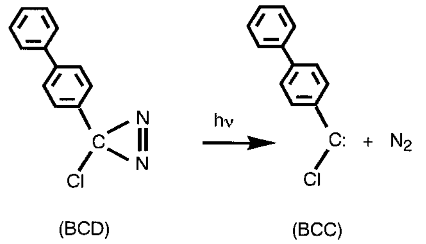
Introduction

Reactions of methylene with electron-deficient olefins, such as fumaronitrile, acrylonitrile, and dimethyl acetylene dicarboxylate, yield pyrrole derivatives in acetonitrile (MeCN).[1−3] These reactions proceed by way of a nitrile ylide (NY) intermediate formed by the addition of methylene to the nitrile solvent. The reactions of 1-naphthylcarbene,[4−6] 2-naphthylcarbene,[7] fluorenylidene,[8,9] and cyclopentadienylidene[10] in MeCN also proceed via NY. On the other hand, chloro(phenyl)carbene, a typical singlet carbene does not form NY.[11,12] Only in the reaction of chloro(4-nitrophenyl)carbene with MeCN could NY be detected spectrometrically.[13]

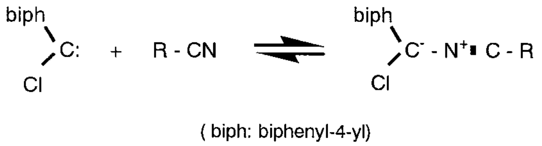


$$\mathrm{H_2C{:}} + \mathrm{R{-}CN} \longrightarrow \mathrm{H_2C^{-}{-}N^{+}{\equiv}C{-}R} \qquad (1)$$

Recently, we detected a long-lived singlet carbene, (biphenyl-4-yl)chlorocarbene [BCC, $\tau = 24.8\ \mu$s in 2,2,4-trimethylpentane], during the laser flash photolyses (LFPs) of (biphenyl-4-yl)chlorodiazirine (BCD) as shown in eq 2.[14] To clarify the NY formation reaction of singlet carbene toward nitrile compounds, we studied the LFPs of BCD.[15] Although we were unable to measure an absorption spectrum of NY, the formation of NY could be kinetically clarified as BCC adducted toward the nitrile compound to form NY in equilibrium, as shown in eq 3.



(2)



$$\mathrm{biph(Cl)C{:}} + \mathrm{R{-}CN} \rightleftharpoons \mathrm{biph(Cl)C^{-}{-}N^{+}{\equiv}C{-}R} \qquad (3)$$

There are two probable structures for NY, the 2-azonia-1-allenide and the 2-azonia-1-propynide structures (Scheme 1). Several papers based on the MO calculations of NY way serve as a means to study the NY structure.[16−20] Houk et al. reported that the latter type formonitrilio methnide ($H{-}C^{-}{=}N^{+}{=}CH_2$) is more stable than the former structure.[17,18]

A matrix isolation method using the IR spectrum is the best way to study the structures of short-lived intermediates and the reaction mechanisms. We investigated many intermediates at low temperature. The structure of NY produced from 3-phenyl-2H-azirine was also reported to be the 2-azonia-1-allenide structure from IR measurements in a 10 K argon matrix.[21] To

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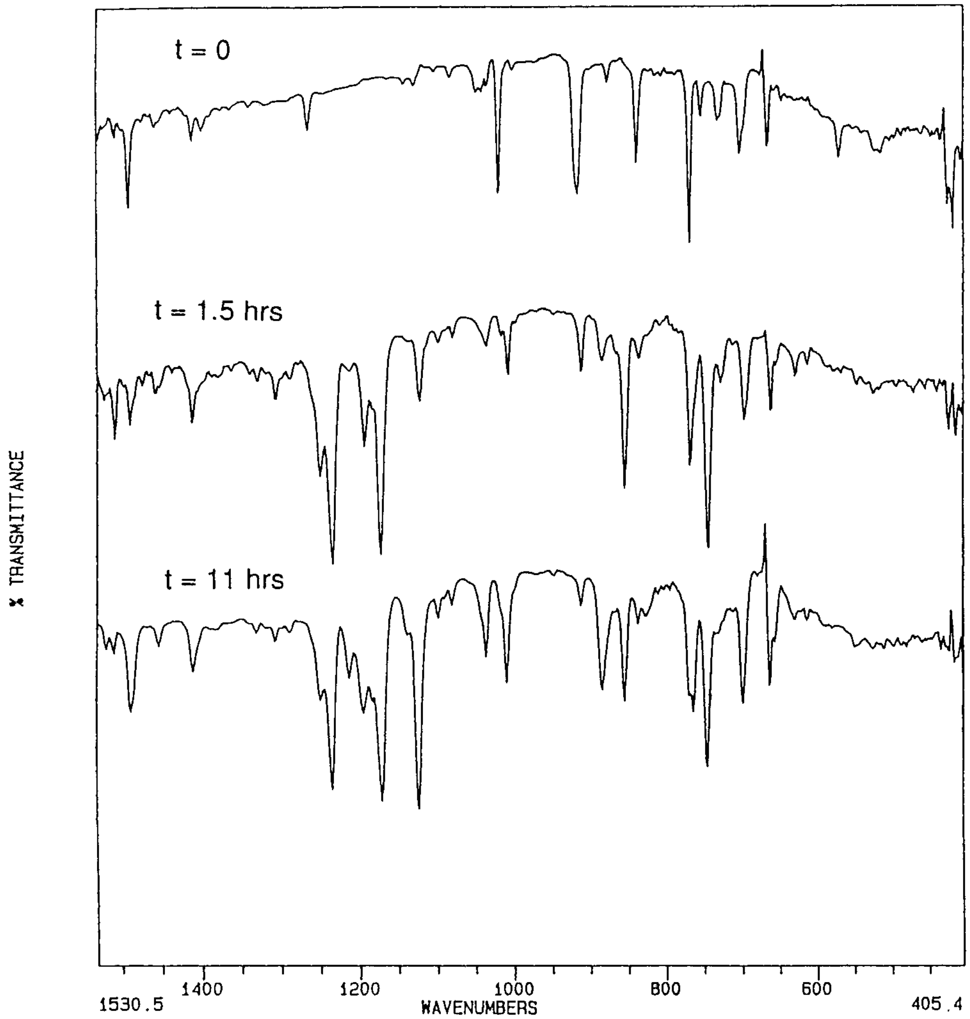
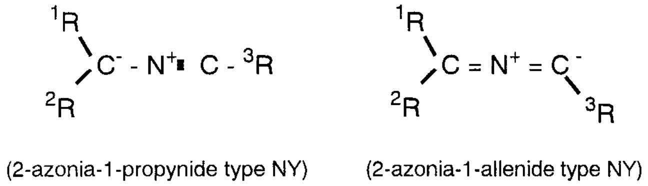


Figure 1. Change of IR spectrum of 10 K BCD−argon matrix in irradiation (1530−405 cm^{-1}). Photoirradiations were carried out using a 150 W xenon lamp. Irradiation time: 0, 1.5, and 11 h.

SCHEME 1: Probable Structures of NY



(2-azonia-1-propynide type NY) (2-azonia-1-allenide type NY)

clarify the NY structure, we studied BCC and NY by means of IR bands in a low-temperature argon matrix and these vibration analyses.

Experimental Section

(Biphenyl-4-yl)chlorodiazirine (BCD) was prepared from 4-cyanobiphenyl via the corresponding amidizine hydrochloride salt (vide infra).8) White crystals: $\lambda_{max} = 358$ nm ($\epsilon = 4.2 \times 10^3$ dm^2 mol^{-1}), 376 nm ($\epsilon = 6.2 \times 10^3$ dm^2 mol^{-1}), and 395 nm ($\epsilon = 5.2 \times 10^3$ dm^2 mol^{-1}) in 2,2,4-trimethylpentane (i-Oc). We used spectroscopic grade MeCN without further purification, as well as argon gas (commercially purified grade) without further purification.

The equipment for the matrix isolation and IR measurements was previously described in detail.[22] The BCD−argon matrices were made by adhesion of BCD with argon gas on a 10 K cesium iodide crystal under high vacuum. The tricomponent matrices were made using an argon−MeCN mixed gas instead of argon gas. The concentrations of BCD and MeCN were determined by means of absorption coefficients [BCD, 4.33×10^3 dm^2 mol^{-1} (1212 cm^{-1}), 1.50×10^3 dm^2 mol^{-1} (912 cm^{-1}); MeCN, 8.15×10 dm^2 mol^{-1} (2296 cm^{-1}), 2.48×10^2 dm^2 mol^{-1} (2258 cm^{-1}) in chloroform]. Photoirradiations of the matrix were carried out using a 150 W or a 500 W xenon lamp. Filters were not used.

The BCC and NY bands were calculated after optimization of the molecular structure by using the Gaussian 94 program.[23] The geometry optimization and vibration frequency calculations were performed at the RHF/6-31G* level of theory.[24]

Results

Photoreaction of BCD−Ar Matrix. The photoirradiation of BCD yields BCC.[14] We studied BCC using the IR spectrum change of the ca. 10 K BCD−Ar matrix in the photoirradiation. The IR spectrum of the matrix before irradiation agreed with those of the BCD KBr disk or BCD carbon tetrachloride solution. The photoirradiations of the matrices were carried out using a 150 W xenon lamp. Figure 1 shows the changes in the IR spectrum of the BCD−Ar matrix during irradiation. Photoirradiation formed many bands. Some bands decreased while the other bands increased with additional irradiation. Table 1 lists the changes in the IR bands during the photoirradiation. With only a 0.5 h irradiation, many new bands were measured, although the bands assigned to BCD still remained. After 1.5 h of irradiation, the BCD bands decreased and the newly measured

TABLE 1: Changes of IR Bands in the Photoirradiation of 10 K BCD−Argon Matrix[c]

before irradiation/ cm$^{-1\,a}$	after irradiation/cm$^{-1\,b}$ 1.5 h	(change)	(11 h change)	remarks
	2047 m	formation	decreased	diazo compound
	1809 w	increased	increased	product
	1796 m	increased	increased	product
	1777 m	increased	increased	product
	1746 w	increased	increased	product
	ca. 1695 m sh	increased		
1618 vs				BCD [1605]
1601 vs				BCD [1605]
1580 m		increased		
1566 m		increased	unclear	product ?
1528 w		decreased		BCD [1526]
	1509 w	formationd	decreased	BCC
1489 m		decreased		BCD [1487]
	1456 w	increased		BCC ?
	sh	new peak	1453 w	Product
	1412 m	formation		BCC
1410 w	sh	decreased	1410	BCD [1408]/ product ?
	1308 mw	formation	decreased	BCC
1264 w		not clear		BCD [1261]
	1250 sh	formation	decreased	BCC
	1235 s	formation	decreased	BCC
		new peak	1214	product
	1194 m	formation	unchanged	products
	1173 s	formation	decreased	BCC
		new peak	1171	product
	1123 s	formation	increased	product
1046 w		decreased		BCD [1035]
	1036 m	formation	increased	product
1017 s		decreased		BCD [1009]
	1007 m	formation		BCC + product
		new peak	1009	product ?
912 s		decreased		BCD [911]
	884 mw	formation	increased	product
874 w		not clear		
	855 s	formation	decreased	BCC
835 s		decreased		BCD [830]
	770 m	formation	decreased	BCC
			764 formation	product
766 s		decreased		BCD [764]
750 w		not clear		BCD [748]
	745 s	formation	increased	product (or with carbene)
729 w		decreased		BCD [721]
700 m	698 m	not clear (shifted ?)		BCD [690]
664 m		unchanged		
	631 w	formation	decreased	BCC
569 w		decreased		BCD [561]
517 w		decreased		BCD [509]
			519	product ?
426 m,sh		decreased		BCD
419 m		decreased		BCD [416]

[a] Adhesion was carried out for 2 h. [b] Photoirradiations were carried out with the aid of a 150 W xenon lamp. In brackets of the remarks, the absorptions of BCD in CCl_4. Intensities of IR band: vs = very strong, s = strong, m = medium, w = weak, mw = rather stronger than weak (w < mw < m), sh = shoulder peak. [c] [BCD] = ca. 1.5 × 10^{-4} mol dm^{-2}.

bands increased. After 4 h irradiation, some of the new bands decreased (assigned to **A**: 2047, 1509, 1412, 1308, 1250, 1235, 1173, 855, 770, and 631 cm^{-1}) and the others increased (assigned to **B**: 1580, 1566, 1453, 1214, 1194, 1171, 1123, 1036, 1009, 884, 764, 745, and 519 cm^{-1}). After 11 h of irradiation, some bands (**A**) completely decreased and other bands (**B**) increased. Further irradiation did not change the spectrum of the matrix. Figure 1 shows the IR spectra of the BCD−Ar matrix before irradiation (1) and after 1.5 (2) and 11 h of irradiation (3) in the range from 1530 to 405 cm^{-1}. The identical results reoccurred three times.

Apparently, photoirradiation of BCD produced the new species (**A**) causing these bands (eq 4). The other species causing these bands (**B**), that looked like a product, is obtained according to the decrease in that species (**A**) (eq 4).

$$\mathrm{BCD} \xrightarrow{h\nu} \mathbf{A} \tag{4}$$

$$\mathbf{A} \longrightarrow \mathbf{B} \tag{5}$$

The major IR bands of phenylchlorocarbene were reported (1590, 1225, 1170, 848, 735 cm^{-1}).[24] Except for the band at 1590 cm^{-1},[25] these reported bands agreed well with the measured bands of **A** (1235, 1173, 855, and 770 cm^{-1}). We assigned these bands (**A**), except for those at 2047 cm^{-1} (**C**) which were assigned to BCC that resulted from the photoirradiation of BCD, because of the good agreement of these measured bands with the calculated bands, as described below.

We also measured the new band at 2047 cm^{-1} (**C**), which decreased during additional irradiation, in the irradiations of the BCD−MeCN−Ar matrix. It is a well-known fact that a part of diazirine yields a diazo compound, which decomposes also to carbene and N_2 gas by photoirradiation. The diazo compounds were reported to have the band around 2050 cm^{-1}.[27−29] We assigned the new band at 2047 cm^{-1} to the diazo compound, (biphenyl-4-yl)chlorodiazomethane (**C**).

According to the decrease of the BCC (**A**) bands, the another bands (**B**) were increased simultaneously. Chloro(phenyl)-carbene yielded chlorocycloheptatetraene by further photoreaction[29] and reacted with other molecules, such as oxygen[29] and carbon dioxide,[30] even in the 10 K argon matrix. When BCC yielded several products by the additional irradiation, the measured bands (**B**) emerged due to these compounds [chlorocycloheptatetraene (1834 w, 1816 w, 1380 s, 773 vs, 690 s, 678 vs cm^{-1}), phenyl chloroformate (1796 s, 1494 s, 1194 s, 1122 s cm^{-1}), and benzoyl chloride (1783 vs, 1743 s, 1453 s, 1210 s, 1176 s, 879 s, 685 m cm^{-1})].[28,30] Because the measured bands (**B**) agreed roughly with those reported bands,[24] BCC seemed to produce the rearranged product, phenylchlorocycloheptatetraene, and oxidation products, (biphenyl-4-yl) chloroformate and 4-(phenyl)-benzoyl chloride, by the reactions with oxygen in argon during the additional irradiation.

Photoreaction BCD−MeCN−Ar Matrix. We studied the reactions of BCC with MeCN based on the IR spectrum changes in the BCD−MeCN−Ar tricomponent matrix, using a 500 W xenon lamp. We determined the concentrations of BCD and MeCN in the matrix by using these absorption coefficients (molar ratio, [MeCN]/[BCD] = 1.8, 2.8, 5.3, 11.3, 13.4). When the ratio was less than 10, we measured the BCC bands (**A**) along with the other new bands (**D**; 1781, 1723, 1591, 1509, 1306, 1291, 1213, 1192, 1184, 1007, 884, 855, 745, 700, 629, 532, and 513 cm^{-1}). The BCC bands decreased with increasing product band (**B**) intensities and with increasing new band (**D**) intensities according to the photoirradiation. When the ratio was larger than 10, the new bands (**D**) could be measured without the bands assigned to BCC (**A**) and to the product (**B**) by the photoirradiation. Figure 2 shows the changes in the IR spectrum of the BCD−MeCN−Ar tricomponent matrix due to the irradiation in the range from 1250 to 405 cm^{-1} ([BCD] = ca. 4.5 × 10^{-4} mol dm^{-2}, [MeCN] = ca. 5.1 × 10^{-3} mol dm^{-2}). Because the new bands (**D**) were stable toward further irradiation

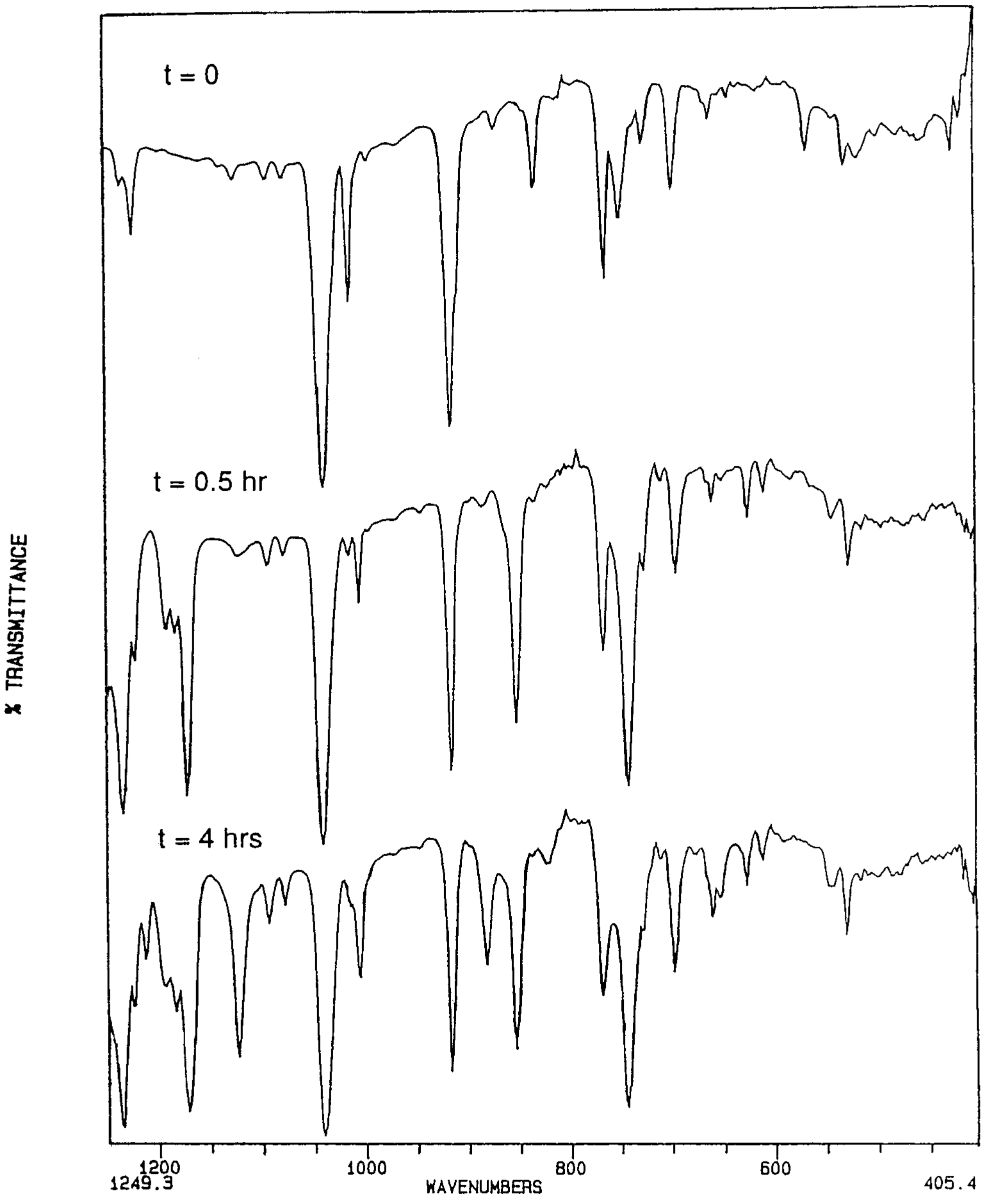


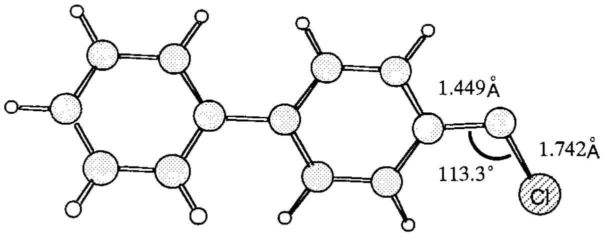
Figure 2. Change of IR spectrum of 10 K BCD−MeCN−argon matrix in irradiation (1250−405 cm^{-1}): [BCD] = ca. 4.5 × 10^{-4} mol dm^{-2}; [MeCN] = ca. 5.1 × 10^{-4} mol dm^{-2}. Photoirradiations were carried out using a 500 W xenon lamp. Irradiation time: 0, 0.5, and 4.0 h.

and toward increasing temperature of the matrix up to ca. 45 K, they seemed to be the bands assigned to the new products. Because these bands agreed well with the 2-azonia-1-allenide type NY calculated using a vibration analysis, the last spectrum of Figure 2 was that of NY (**D**). BCC yielded the allenyl-type NY by the addition to nitrile compounds even in the ca. 10 K Ar matrix (eq 6).

$$\mathbf{A}\ (\mathbf{BCC}) + \mathrm{MeCN} \longrightarrow \mathbf{D}\ (\mathbf{NY}) \qquad (6)$$

Vibration Analysis. The optimization of the structure was carried out using the number of atoms (BCC: $C_{13}H_9Cl$) and the approximate coordinates of the atoms. The optimized BCC structure is illustrated in Scheme 2. The angle (∠biphenyl−C−Cl = 113.3°) and bond lengths ($r_{\text{biphenyl ring−C}}$ = 1.45 Å, $r_{\text{C−Cl}}$ = 1.74 Å) of the optimized geometry are demonstrated in this scheme. Using the BCC structure, we calculated the vibration frequencies, as listed in Table 3. It is a well-known fact that the measured bands agreed well with the calculated band after modification using the factor 0.9.[31] Because the modified bands (frequency and its intensity) agreed fairly well with the measured bands (**A**: 1509, 1412, 1308, 1235, 1173, 855, 770, and 631 cm$^{-1,33}$), they were assigned to BCC. BCD decomposed to BCC due to irradiation in the ca. 10 K argon matrix.

SCHEME 2: Optimized Structure of bcc



(< two benzene ring = 43.2°)

We carried out a similar optimization for the NY structure produced by the addition of BCC to MeCN. The obtained geometry is illustrated in Scheme 3. There are two probable structures for NY, 2-azonia-1-allenide and the 2-azonia-1-propynide structures. The numbers in Scheme 3 show the carbon atoms from the carbene center (1), from the nitrile group (2),

TABLE 2: Change of IR Bands of 10 K BCD−MeCN−Ar Matrix in the Photoirradiation[c]

before irradiation/ $cm^{-1\,a}$	after irradiation/$cm^{-1,b}$			
	0.5 h	(change)	(4 h change)	remarks
	2047 s	formed	decreased	diazo compound
	1781 w	formed	increased	NY
	1723 s	increased	unchanged	NY
1717 m	1717 m	unchanged	unchanged	
1615 m	1615 m	unchanged	unchanged	NY + MeCN ?
1604 vs	1603 vs	unchanged	unchanged	
	1591 vs	formed	unchanged	NY
1578 s		undetectable		
	1509 w	formed	slightly increased	NY
1489 s	1489 w	decreased	unchanged	
1449 vs	1447 vs	unchanged	unchanged	MeCN [1439]
1410 vs	1410 vs	unchanged	unchanged	
1377 vs	1377 vs	unchanged	unchanged	MeCN [1377]
1364 s,sh	1364 s,sh	unchanged	unchanged	
	1306 m	formed	slightly increased	NY
	1291 w	formed	unchanged	NY
1264 m	1264 m	unchanged	unchanged	
	1235 vs	formed	unchanged	NY
1223 m	1223 m	unchanged	unchanged	
	ca. 1213 w	formed	increased	NY
	ca. 1192 m	formed	unchanged	NY
	ca. 1184 m	formed	unchanged	NY
	1173 vs	formed	unchanged	NY
1042 vs	1042 vs	nchanged	unchanged	MeCN [1038]
1017 s		undetectable		
	1007 m	formed	increased	NY
918 vs	918 vs	unchanged	unchanged	MeCN [919]
	884 w	formed	increased	NY
	855 vs	formed	unchanged	NY
835 m		undetectable		
766 s	770 s	unchanged	unchanged	MeCN [748]
750 m		undetectable		
	745 vs	formed	unchanged	NY
729 w	729 m	increased	unchanged	MeCN [748]
700 m	698 m	unchanged	increased	NY
664 w	664 w	unchanged	increased	MeCN [629]
	629 w	formed	increased	NY
569 w	569 w	decreased	unchanged	
	532 w	formed	increased	NY
525 w	525 w	decreased		
	ca. 513 w	formed	increased	NY
428 w	428 w	unchanged	undetectable	
ca. 418 w	ca. 418 w	unchanged	undetectable	

[a] Adhesion was carried out for 2 h. [b] Photoirradiations were carried out by an aid of a 500 W xenon lamp. Intensities of IR band: vs = very strong, s = strong, m = medium, w = weak, mw = rather stronger than weak (w < mw < m), sh = shoulder peak. [c] [BCD] = ca. 4.5×10^{-4} mol dm^{-2}; [MeCN] = ca. 5.1×10^{-3} mol dm^{-2}.

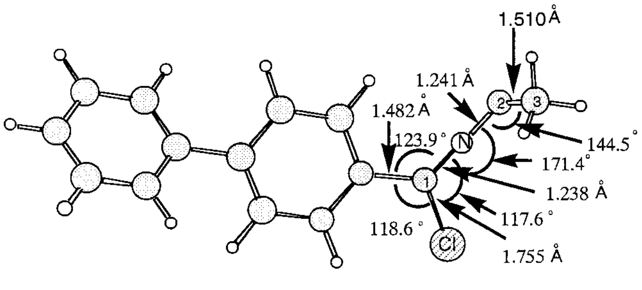
and from the methyl group (3) of MeCN. The structure of NY is easily distinguishable by using typical bond angles. The 2-azonia-1-propynide structure is characterized by the angles around the N atom (∠C(1)NC(2)) and around the C atom from the nitrile group (∠NC(2)C(3)). Both are 180°. On the other hand, the 2-azonia-1-allenide structure is characterized by the angle between the two double bond surfaces (∠C(1)N−NC(2)). We calculated the bond angle between the two double bond surfaces in the optimized structure to be 90.5° and around the C atom from the nitrile group to be 144.5°. The bond angle around the N atom, 171.4°, also agreed well with the calculated value for $CH_2{=}N^+{=}CH^-$ structure (171°,[17] 157°,[18]). Houk et al. reported that the 2-azonia-1-allenide type NY is more stable than the 2-azonia-1-propynide type NY [93.6 kJ mol^{-1} (STO-3G), 68.6 kJ mol^{-1} (MINDO/3)].[18] We conclude that the optimized structure of NY is the 2-azonia-1-allenide.

TABLE 3: Calculated bcc IR Bands by Means of RHF/6-31G* Basis Set (Int. > 0.10 KM mol^{-1})

calculated band/cm^{-1}	modified band/cm^{-1a}	intensity/ KM mol^{-1}	measured band/cm^{-1b}	remarks
440.8	392	0.127	?	
688.9	613	0.154	631 w	
778.0	672	0.217	698 m	overlapped with BCD band?
803.7	715	2.429	745 s	overlapped with product band?
814.2	725	0.180	?	
826.8	768	0.471	770 m	
926.7	825	1.052	855 s	
963.0	857	0.368	884 mw	overlapped with product band?
1098.9	978	0.163	1007 m	
1220.7	1086	0.560	1123 s	overlapped with product band?
1295.1	1153	3.370	1173 s	
1306.0	1162	0.165	?	
1310.8	1167	0.160	?	
1337.3	1190	0.139	?	
1350.5	1202	3.013	1235 s	
1447.5	1288	0.153	1308 mw	
1551.7	1381	0.359	1412 m	
1681.5	1497	0.327	1509 w	
1729.2	1539	0.143	1566 m	overlapped with BCD band?
1789.1	1592	3.855	1601 s	overlapped with BCD band?
1810.2	1611	0.152	?	
3376.8	3005	0.289	?	
3386.8	3014	0.286	?	
3393.5	3020	0.235	?	

[a] Frequencies of modified band have been multiplied by a factor of 0.9. [b] Measured intensities of IR band: vs = very strong, s = strong, m = medium, w = weak, mw = rather stronger than weak (w < mw < m).

SCHEME 3: Optimized Structure of NY



(< two benzene ring = 44.6°, < ^{1}CCl - ^{2}C^{3}C = 90.5°)

We calculated the bands and their intensities using a vibration analysis, as listed in Table 4. The intensities of the calculated bands and modified frequencies agreed well with the measured bands (1591, 1509, 1410, 1306, 1235, 1213, 1192, 1184, 1173, 1007, 884, 855, 745, 700, and 629 $cm^{-1,32)}$) except the relatively strong modified band at 1086 cm^{-1} (intensity = 0.560 KM mol^{-1}). We conclude that NY has an 2-azonia-1-allenide geometry.

Conclusions

We studied the formation of NY by the addition of BCC to MeCN by using low-temperature Ar matrices. After photoirradiations of the BCD−Ar matrix, we measured the IR bands of BCC. These bands agreed fairly well with the calculated bands. We also studied the photoirradiation of the BCD−MeCN−Ar tricomponent matrices. When the molar ratio, [MeCN]/[BCD],

TABLE 4: Calculated NY Bands by Means of RHF/6-31G* Basis Set (Int. > 0.10 KM mol^{-1})

calculated band/cm^{-1}	modified band/cm^{-1} [a]	intensity/ KM mol^{-1}	measured band/cm^{-1} [b]	remarks
580.0	516	0.111	532 w	
688.9	613	0.154	629 w	
778.0	672	0.217	700 m	
803.7	715	2.429	745 s	
814.2	725	0.180	?	
826.8	768	0.471	770 s	overlapped with MeCN band
926.7	825	1.052	855 s	
963.0	857	0.368	884 m	
1098.9	978	0.163	1007 m	
1220.7	1086	0.560	?	
1295.1	1153	3.370	1173 s	
1306.0	1162	0.165	1184 m	
1310.8	1167	0.160	1192 m	
1337.3	1190	0.139	ca. 1213 w	
1350.5	1202	3.013	1235 vs	
1447.5	1288	0.153	1306 m	
1551.7	1381	0.359	1410 vs	overlapped with MeCN band
1681.5	1497	0.327	1509 w	
1729.2	1539	0.143	?	
1789.1	1592	3.855	1591 vs	
1810.2	1611	0.152	?	
3376.8	3005	0.289	?	
3386.8	3014	0.286	?	
3393.5	3020	0.235	?	

[a] Frequencies of modified band have been multiplied by a factor of 0.9. [b] Measured intensities of IR band: vs = very strong, s = strong, m = medium, w = weak, mw = rather stronger than weak (w < mw < m).

was less than 10, we measured the new bands along with the BCC bands. For [MeCN]/[BCD] >10, we measured only the new bands without the presence of the BCC bands. They appear to be due to NY. We optimized the NY structure as the 2-azonia-1-allenide geometry using the RHF/6-31G* basis set. The bands calculated for this structure agreed with the new bands. NY was immediately produced after the formation of BCC by annealing the matrix even at 10 K.

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(31) The intensities of the IR bands are indicated by vs (very strong), s (strong), m (medium), and w (weak). The sh showed shoulder peak.

(32) Ammann used 0.89 as a scale factor on the vibration analysis of *o*-tolylfluorocarbene by means of HF/6-31G* basis set. Ammann, J. R. *I. Matrix Isolation Study of Alkyl Substituted Ground-State Singlet Carbenes II. Characterization and Reactivity of o-Tolylhalocarbenes*; UMI A Bell & Howell Information Company: MI, 1997; p 211.

(33) When the measured band seems to be overlapped with other band, that band is ruled out, though the calculated band is corresponding to that band.