Polish J. Chem., **74**, 1723–1730 (2000)

Evidence for the Formation of Diisocyanodiacetylene in Argon Matrices

by R. Kołos

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

(Received July 25th, 2000)

Dicyanodiacetylene, N≡C-C≡C-C≡C-C≡N was dissociated by (*i*) laser photolysis at 193 nm and (*ii*) electrical discharges through its mixture with argon. The products, isolated in cryogenic matrices, were analysed by IR spectroscopy. In addition to the bands recently assigned to cyanoisocyanodiacetylene, another group of mutually correlated spectral features has been found. Its carrier is tentatively identified as diisocyanodiacetylene based on *ab initio* and density functional theory calculations.

Key words: matrix isolation, cyanoacetylenes, interstellar molecules

Dicyanopolyacetylenes, N≡C-(C≡C)$_n$-C≡N, rod-like molecules built of similar weight atoms, deserve the attention of spectroscopists as interesting systems *per se* and as potential constituents of the interstellar matter [1]. The photochemistry of $n = 1$ species, dicyanoacetylene, N≡C-C≡C-C≡N (DCA), has been studied both in the gas phase (where it was shown to decompose into CN and CCCN radicals [*e.g.* 2,3,4]) and in rare gas matrices [5,6], where its two-photon conversion into cyanoisocyanoacetylene, :C=N-C≡C-C≡N (CICA), was observed. The $n = 2$ compound, dicyanodiacetylene, N≡C-(C≡C)$_2$-C≡N (DCDA), is known since 1920 when it was synthesized by Moureu and Bongrand [7]. The photochemical work on this exotic molecule is limited to the recent IR study by Kołos [8], who postulated that 248 nm photolysis efficiently transforms the matrix-isolated DCDA into its *monoiso* version, cyanoisocyanodiacetylene, :C=N-(C≡C)$_2$-C≡N (CICDA), – in a perfect analogy to the DCA behaviour found by Smith *et al.* [5]. This tentative assignment has been confirmed with advanced CCSD(T) calculations by Botschwina and Oswald [9].

This paper reports on further transformations of matrix-isolated DCDA with more energetic photons and with electrical discharges.

EXPERIMENTAL

Dicyanodiacetylene was synthesized following the procedure of Miller and Lemmon [10], starting with methyl propiolate. The compound was kept in the presence of P_2O_5 and resublimed before each experiment.

The 1:2500 mixtures of DCDA and argon (Aldrich, 99.998%; typical quantity: 2 millimols), were sprayed onto a cold (12–14 K) CsI substrate window inside an Air Products *Displex* closed-cycle helium refrigerator. Two distinctly different procedures were utilized (*i*) UV laser photolysis of solid matrices

and (*ii*) electrical discharges through gaseous mixtures prior to their condensation into solids. *193 nm photolysis*: This experiment consisted in the irradiation of the matrix with an attenuated ArF excimer laser beam (Lambda Physik EMG 101, running at 1.5 Hz). Approximately 10^4 laser pulses, each bearing the energy of 1 to 2 mJ/cm^2 were applied. *Electrical discharge*: The cold-window-radial-discharge (CWRD) arrangement used in this part of the study has been described elsewhere [11]. Briefly, a high voltage electrode tip was inserted into a small orifice in the substrate window centre (Fig. 1). This allowed to establish – during the gas mixture deposition (with a flow rate of *ca.* 1 mmol/h) – a corona-type electric discharge covering the surface between the central orifice and the grounded circular frame of the window.

The absorption spectra of solid samples produced by both techniques were recorded in IR with a Nicolet 170 SX Fourier transform instrument (typical resolution 0.25 cm^{-1}) and in the UV/Vis region with Shimadzu UV-3100 spectrophotometer.

Quantum chemical calculations were done with the GAUSSIAN 98 software package [12].

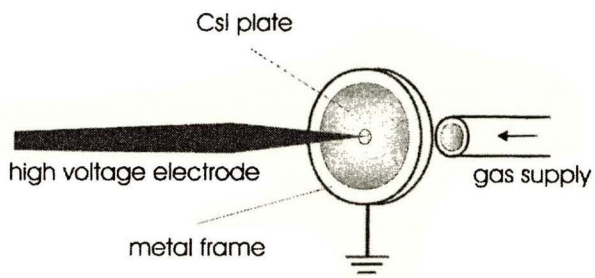

Figure 1. Schematic view of the electrical discharge arrangement (CWRD). The circular copper frame of the CsI window is attached to the cold finger of the cryostat and held at ground potential. The electrode supplies approximately 10 kV of oscillating voltage, its tip is introduced into the orifice (diameter *ca.* 0.5 mm) drilled in the window centre. On the surface of the opposite side of the window, between the orifice and the metal frame, the glow discharge is established when the gas flows.

RESULTS AND DISCUSSION

Photolysis: The choice of 193 nm as the photolysis wavelength was partly suggested by the former photochemical work on shorter analogues of DCDA. Namely, the gas phase experiments of Halpern *et al.* [2] pointed to 200 nm and 232 nm as thresholds of CN production from cyano- and dicyanoacetylene, respectively.

The exact shape of the strong $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ DCDA vacuum-UV absorption band in argon matrices is not known. Still, it is clear from the gas phase work by Connors *et al.* [13] that 193 nm radiation coincides with the long-wavelength slope of this band. Somewhat to our surprise, however, the IR bands of the products were almost absent after the ArF laser photolysis. Presuming that this might be due to the filtering of incoming radiation by photolysis products, we decided to perform the irradiation "layer by layer". After spraying a small portion of the gas mixture (typically 2% of the total volume) onto the substrate plate and waiting for *ca.* 30 s (to assure the thermal equilibration of the sample) a short photolysis session was performed – and the next cycle started. This resulted in a remarkable rise of product bands intensity. (The filter effect of this kind was not important in former 248 nm photolysis experiments [8]). Then it

was checked that essentially identical spectra were generated, even more efficiently, when the irradiation took place during the *continuous* deposition with a gas flow of *ca.* 1 mmol/h. (The direct photolysis of gaseous DCDA had to be negligible in such experiments; the comparison of a laser pulse width and the repetition rate indicates that just 1 out of *ca.* 10^8 molecules, heading from the nozzle to the substrate plate could interact with UV photons).

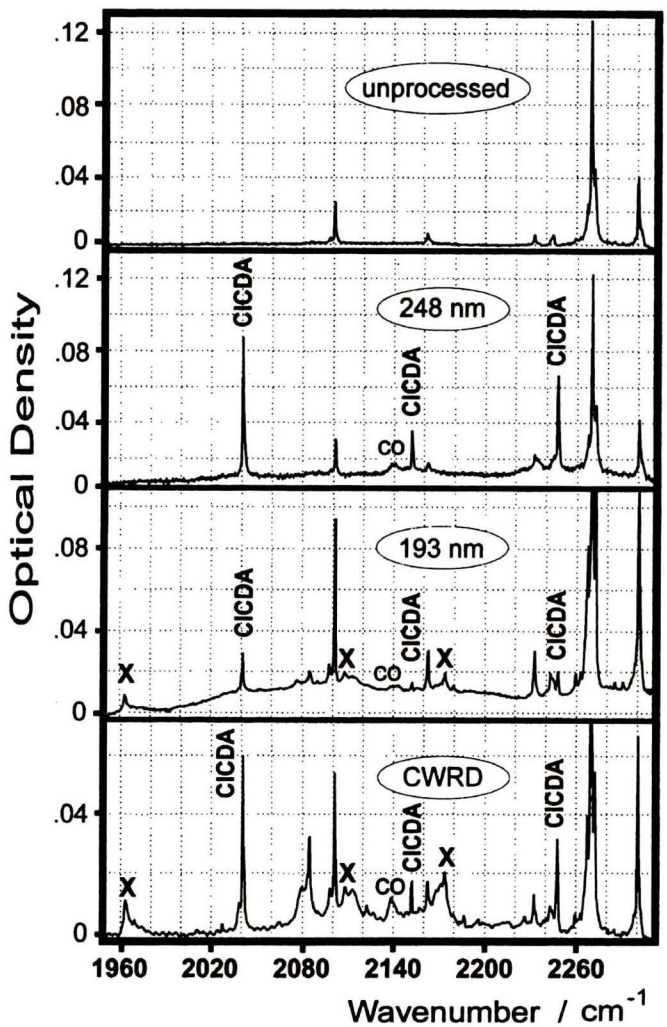

Figure 2. Triple bond stretching region in IR absorption spectra of dicyanodiacetylene isolated in argon matrices: unprocessed sample (topmost), after 248 nm photolysis [8], after 193 nm photolysis and (bottom) trapping of electrical discharge products. The relative efficiencies of three conversion methods can be estimated by comparing the intensities of product bands to those of the precursor compound. **X** denotes a set of spectral features (see text).

The set of IR spectral features with correlated intensities was clearly discernible among product bands. These bands, several times stronger than in the present study, were already observed in the course of the 248 nm photolysis of DCDA [8] (*cf.* middle panels of Fig. 2) and assigned to CICDA fundamental frequencies. The present spectrum is more complicated, however. Additional, weaker features were developed apart from those of CICDA. Because of the higher signal-to-noise ratio and overlapping broader bands, the intensity correlations, when found, were not as unambiguous as for CICDA fundamentals. A good correlation, however, was found for bands marked as **X** in Fig. 2. The intensities of other IR features listed in Table 1, *e.g.* 2084.9 cm^{-1} or 2090.2 cm^{-1} are not related to the ones of CICDA or of set **X**, neither their mutual intensity correlations could be established. No IR bands became more intense upon annealing of the sample at 35 K (rather, a slight decrease of intensity was noticed).

Table 1. IR product bands developed during photolysis and discharge treatment of dicyanodiacetylene.

Wavenumber (cm^{-1})[a]	Method of generation[b]	Remarks
1963.8	ArF, CWRD	set X[c]
1969.6	CWRD	
2027.4	CWRD	
2041.1	ArF, KrF, CWRD	CICDA[d]
2076.6	ArF, CWRD	
2080	CWRD	*broad*
2083.2	ArF, CWRD	
2084.9	ArF, CWRD	
2090.2	CWRD	
2108.1	ArF, CWRD	set X
2113	ArF, CWRD	*broad*
2122.5	CWRD	
2151.8	ArF, KrF, CWRD	CICDA
2172	ArF, CWRD	*broad*
2173.6	ArF, CWRD	set X
2186.2	ArF, CWRD	
2247.4	ArF, KrF, CWRD	CICDA

[a]accuracy ≥ 0.2 cm^{-1}; [b]ArF and KrF symbols refer to the photolysis at 193 nm (this work) and at 248 nm [8], respectively; CWRD denotes the electrical discharge experiment; [c]set of mutually correlated bands (see text); [d]assignment postulated in [8].

The 22.7 and 24.7×10^3 cm^{-1} electronic bands developed during the photolysis (generated also by Smith *et al.* in electrical discharges through DCA [14] and tentatively assigned to C_5N_2) were – contrary to the IR features – more intense after the 193 nm photolysis than after 248 nm photolysis.

Electrical discharges: Infra-red spectra resulting from the CWRD treatment of DCDA (Fig. 2, bottom panel) were quite similar to those developed in 193 nm photolysis. The same intensity correlations were observed, allowing to distinguish the CICDA and **X** sets of bands. Other bands listed in Table 1 often showed up in both CWRD and photolysis experiments.

Likewise, apart from the strong absorption of CN radical at 25.9×10^3 cm^{-1}, the electronic spectra of samples prepared by CWRD were similar to those generated dur-

ing the 193 nm photolysis. The *simultaneous* measurement of vibrational and electronic spectra, resulting from discharges, could only be done once, for an extremely diluted sample (when we ran almost out of stock DCDA). In this experiment the IR features of the parent compound were some 30 times weaker than usually. Accordingly, only minute traces of CICDA bands and no **X** features were detected. However, the intensity of some other previously observed IR product bands, in particular those at 2076.6 cm^{-1} and 2084.9 cm^{-1} was quite high and, interestingly, the visible bands at 22.7 and 24.7×10^3 cm^{-1} were also strong.

The qualitative comparison of the intensities of generated IR and UV/Vis bands (both in the photolysis and discharge experiments) strongly suggests that UV/Vis features – prominent after CWRD treatment, less pronounced after 193 nm photolysis and weak after 248 nm photolysis – correlate neither with CICDA nor with **X** bands in IR. On the other hand, the relation of these electronic bands to some other IR features listed in Table 1 seems possible.

Within the bulk of rare gas matrices the only conceivable transformations of a hydrogen-less molecule like DCDA are ionization and isomerization (neglecting the reactions with impurities). Indeed, the isomerization of DCDA to CICDA was found as a result of the 248 nm photolysis [8] and has also been revealed by this study. On the other hand, no electronic bands of $C_6N_2^+$ cations (reported by Agreiter *et al.* [15] and Fornay *et al.* [16]) were detected. Since the photolysis at 193 nm generated, apart from CICDA bands, additional spectral features, it seemed justified to expect the formation of yet another obvious rearrangement product, namely diisocyanodiacetylene :C=N-(C≡C)$_2$-N=C: (DICDA). Small quantities of the analogue centrosymmetrical molecule, diisocyanoacetylene :C=N-C≡C-N=C:, photochemically generated from DCA, were found by Smith *et al.* [5].

To decide which IR features could originate from vibrational transitions of DICDA, results of a recent [1] second-order Moeller-Plesset perturbation theory calculations (6-31G* basis set) were recalled. Additional quantum chemical calculations were performed at the density functional theory level (BLYP and B3LYP variants; 6-311+G* basis set). DCDA has been included in this study to test the capabilities of theoretical methods employed. The popular hybrid B3LYP functional seems less accurate than BLYP in the present case (Table 2). This observation coincides with the recent finding of Botschwina and Oswald [9], who noticed BLYP superiority over B3LYP in reproducing the electric dipole moment of CICDA. The frequencies given by BLYP match the experimental values reasonably well, with the exception of ν_6 asymmetric stretch; this particular frequency (and the corresponding intensity) is poorly reproduced by both DFT and MP2 calculations. The band intensity patterns generated by BLYP and by MP2 are not satisfactory and quite different one from the other. It can be remarked, however, that the predictive power of computations seems to be enhanced, when the results of both MP2 and BLYP are taken into account (*e.g.* bands for which the two methods predict higher intensities are indeed strong).

Table 2. Calculated (harmonic) and observed fundamental vibrations of dicyanodiacetylene.

mode/ symmetry	MP2 6-31G* [1]		B3LYP 6-311+G*		BLYP 6-311+G*		experimental (IR, Raman; vapour) [10]	
	harmonic frequency (cm^{-1})	IR intensity (km/mol)	harmonic frequency (cm^{-1})	IR intensity (km/mol)	harmonic frequency (cm^{-1})	IR intensity (km/mol)	frequency (cm^{-1})	IR intensity*)
ν_{13}/π_u	**65**	**6**	**65**	**6.1**	**64**	**5.8**	**62**	*vs*
ν_{12}/π_g	168	0	174	0	169	0	170	
ν_{11}/π_u	**265**	**5**	**317**	**6.8**	**307**	**6.1**	**276**	*vvs*
ν_{10}/π_g	448	0	499	0	481	0	455	
ν_9/π_u	**496**	**6**	**582**	**1.2**	**558**	**1.0**	**491**	*vs*
ν_8/σ_g	468	0	476	0	468	0	501	
ν_7/π_g	507	0	625	0	582	0	571	
ν_6/σ_u	**909**	**1**	**927**	**0.5**	**911**	**1.0**	**717**	*s*
ν_5/σ_g	1314	0	1337	0	1323	0	1288	
ν_4/σ_u	**2039**	**6**	**2182**	**0.2**	**2077**	**0.8**	**2097**	*m*
ν_3/σ_g	2124	0	2285	0	2181	0	2183	
ν_2/σ_g	2208	0	2325	0	2198	0	2235	
ν_1/σ_u	**2229**	**3**	**2364**	**70**	**2251**	**57**	**2266**	*s*

*)s – strong, m – medium, v – very.

DICDA, according to the calculations, is a linear compound, just like CICDA and the parent DCDA, less stable than DCDA by 65.7 kcal/mol (MP2) or 53.2 kcal/mol (BLYP). The calculations (Table 3) give a characteristic pattern of its IR spectrum with just two outstandingly strong features, either of 1:1 (MP2) or of 2.8:1 (BLYP) intensity ratio; other IR-active fundamental bands are predicted to be of at least one order of magnitude lower intensity. These results point to DICDA as responsible for **X** bands at 1963.7 and 2173.6 cm^{-1}; the calculated frequency values are higher by not more than 5% (MP2) or 2% (BLYP). One of the explanations for the presence of the band at 2108 cm^{-1}, which apparently also belongs to set **X**, is a combination mode of overall π_u symmetry, *i.e.* $\nu_3 + \nu_{13}$. The final identification of DICDA in argon matrices and the assignment of its IR bands should be possible when the results of higher level calculations become available. The strong absorption of 193 nm radiation by photolysis products, possibly by CICDA, suggests the two photochemical steps of the diisonitrile formation: DCDA → CICDA → DICDA. Naturally, the back photoreaction of CICDA should be more effective than its transformation into DICDA. This, however, can be compensated by the relative ease of DICDA detection; the calculations predict its IR transition intensities to be *ca.* 2 times higher than for CICDA and 1–2 orders of magnitude higher than for DCDA. The exceptionally low threshold for DICDA detection in IR could also explain the apparent lack of correlated electronic bands.

Additional conclusion – drawn from the unexpectedly rich IR spectrum of 193 nm photolysis products –is that other compounds, apart from izonitriles, are generated. It can probably be rationalized in terms of a strong absorption of the 193 nm laser beam by the photolyzed sample. This characteristic could lead to a transient thermal softening of the matrix surface upon pulse photolysis, thus allowing for some photoinduced reactions normally inefficient within the rigid bulk of rare gas solids.

Such an effect, amplified by the layer-by-layer irradiation technique, could finally give rise to compounds other than CICDA or DICDA. The unassigned bands were particularly strong in CWRD experiments – indicating the preferential formation of their carriers in discharges. According to the meticulous study by Smith *et al.* [14], who isolated the species formed in discharges of isotopically labelled DCA, the 22.7×10^3 cm^{-1} and 24.7×10^3 cm^{-1} electronic bands are generated by a compound with 2 equivalent nitrogen atoms and at least 4 carbon atoms. Whether the identity of this compound is C_5N_2, as proposed by Smith *et al.*, remains an open issue, to be answered by further studies.

Table 3. Calculated (harmonic) fundamental vibrations of diisocyanodiacetylene compared to the measured values.

mode/ symmetry	MP2 6-31G* [1]		B3LYP 6-311+G*		BLYP 6-311+G*		experimental ("X" bands in Ar matrix)	
	harmonic frequency (cm^{-1})	IR intensity (km/mol)	harmonic frequency (cm^{-1})	IR intensity (km/mol)	harmonic frequency (cm^{-1})	IR intensity (km/mol)	frequency (cm^{-1})	IR intensity*)
ν_{13}/π_u	72	4	71	3.0	68	3.5		
ν_{12}/π_g	161	0	175	0	168	0		
ν_{11}/π_u	261	2	272	2.0	264	2.4		
ν_{10}/π_g	401	0	413	0	399	0		
ν_9/π_u	425	0	477	0.2	442	0.0		–
ν_8/σ_g	484	0	493	0	483	1.8		–
ν_7/π_g	567	0	520	0	473	0		–
ν_6/σ_u	971	14	994	12	968	6.5		–
ν_5/σ_g	1366	0	1387	0	1363	0		–
ν_4/σ_u	**2034**	**135**	**2080**	**464**	**1970**	**350**	**1964**	**1**
ν_3/σ_g	2101	0	2135	0	2023	0		–
ν_2/σ_u	**2280**	**141**	**2321**	**244**	**2223**	**127**	**2174**	**1**
ν_1/σ_g	2288	0	2334	0	2227	0		–

*)arbitrary units, accuracy *ca.* ±15%.

CONCLUSIONS

The formation of a centrosymmetrical diisonitrile (DICDA) in 193 nm photolysis and in CWRD discharge experiments is suggested by the comparison of IR spectra with predictions of *ab initio* and DFT calculations. The fact that additional products, apart from isonitriles, are created during the 193 nm photolysis (seemingly contradicting the matrix cage effect), can probably be explained by the local softening of the solid sample upon efficient UV absorption.

Acknowledgment

The work was supported by the Polish State Committee for Scientific Research, grant No. 3 T09A 122 09. The author is grateful to Professor P. Botschwina from the University of Göttingen for the results of his theoretical study on CICDA, prior to the publication.

REFERENCES

1. Kołos R. and Grabowski Z.R., *Astrophys. Space Sci.*, **271**, 65 (2000).
2. Halpern J.B., Miller G.E., Okabe H. and Nottingham W., *J. Photochem. Photob. A: Chemistry*, **42**, 63 (1988).
3. Halpern J.B., Petway L., Lu R., Jackson W.M. and McCrary V.R., *J. Phys. Chem.*, **94**, 1869 (1990).
4. Kołos R., Zieliński Z., Grabowski Z.R. and Mizerski T., *Radiat. Phys. Chem.*, **39**, 159 (1992).
5. Smith A.M., Schallmoser G., Thoma A., Bondybey V.E., *J. Chem. Phys.*, **98**, 1776 (1993).
6. Smith A.M., Bondybey V.E., Horn M. and Botschwina P., *J. Chem. Phys.*, **100**, 765 (1994).
7. Moureu C. and Bongrand J., *Ann. Chim.*, **14**, 47 (1920).
8. Kołos R., *Chem. Phys. Letters*, **299**, 247 (1999).
9. Botschwina P. and Oswald R., *Chem. Phys. Letters*, **319**, 587 (2000).
10. Miller F.A. and Lemmon D.H., *Spectrochim. Acta*, **23A**, 1415 (1967).
11. Kołos R., *Chem. Phys. Letters*, **247**, 289 (1995).
12. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Zakrzewski V.G., Montgomery Jr. J.A., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Strain M.C., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Ortiz J.V., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Gomperts R., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Gonzalez C., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Andres J.L., Gonzalez C., Head-Gordon M., Replogle E.S. and Pople J.A., (1998), *Gaussian 98, Revision A.3*, Gaussian, Inc., Pittsburgh PA.
13. Connors R.E., Roebber J.L. and Weiss K., *J. Chem. Phys.*, **60**, 5011 (1974).
14. Smith A.M., Engel C., Thoma A., Schallmoser G., Wurfel B.E. and Bondybey V.E., *Chem. Physics*, **184**, 233 (1994).
15. Agreiter J., Smith A.M. and Bondybey V.E., *Chem. Phys. Letters*, **241**, 317 (1995).
16. Fornay D., Freivogel P., Fulara J. and Maier J.P., *J. Chem. Phys.*, **102**, 1510 (1995).